THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVIII JULY 1953 No. 7

CONTENTS:

Secretary's Notice - - - - - - - - - - - 367

The Chemistry of Vegetable Tannins IX. Quebracho
By ROBERT C. PUTNAM and JOHN C. ROCKETT - 368

Studies in Chrome Tanning XIX. Further Studies in the Neutralization of Chrome Tanned Leather
By EDWIN R. THEIS and W. R. LOTZ - - 374

Studies in Chrome Tanning XX. Further Studies in the Use of Syntan in Chrome Tanning
By W. R. LOTZ and EDWIN R. THEIS - - 388

The Problem of Tannery Waste Disposal
By HARRY H. REDLICH - - - - - 422

Abstracts - - - - - - - - - - - - - 436

SUBSCRIPTION: Members $12.00 a Year Non-Members $15.00

Published Monthly by

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLICATION OFFICE, EASTON, PA.

Entered as Second-Class Matter at Post Office, Easton, Pa.
Acceptance for Mailing at Special Rate of Postage as Provided for in Section 1103.
Act of October 3, 1917, Authorized July 16, 1918

COPYRIGHT, 1953, THE AMERICAN LEATHER CHEMISTS ASSOCIATION

Reliable Direct Sources the World Over

FOR

VEGETABLE TANNING MATERIALS

WATTLE EXTRACT
WATTLE BARK
MANGROVE BARK
MYRABOLAMS & EXTRACT
VALONEA & EXTRACT
DIVI DIVI
CUTCH
QUEBRACHO
SUMAC— LEAF & GROUND
TARA—PODS & POWDER
OAKWOOD EXTRACT, Swedish
LARCHBARK EXTRACT, Swedish

The Olson Sales Agency, Inc.

Import · Export

20 BROAD STREET (NEAR WALL STREET) NEW YORK 5, N. Y.

Cable Address:
"COROSAGE"

Telephones:
DIGBY 4-0226
0227

I

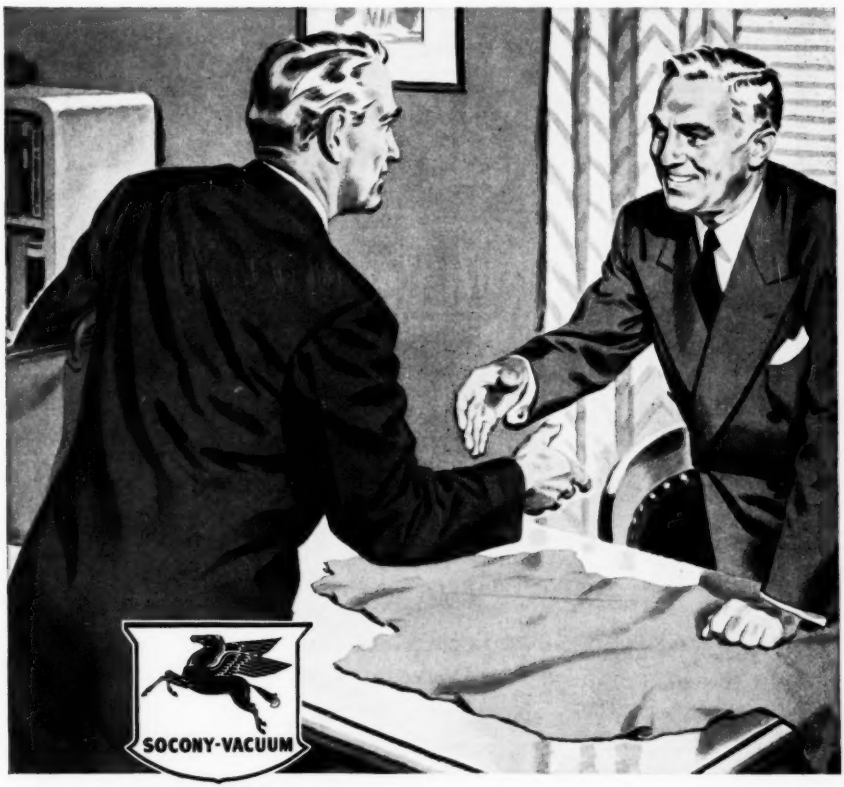
Every one of our field technicians has spent his entire business life working with tanners!

IT'S A LIFETIME JOB...

When you call in one of our field technicians, you can do it with full confidence that he knows his job thoroughly . . . knows your problems and can help you solve them. That's because every one of these men has spent the better part of his life working with the leather industry.

Each is a specialist in leather oils and their correct application. Each is backed by our 87 years of experience . . . our complete research facilities . . . our tested quality products.

Why not consult your Socony-Vacuum Representative for help with *your* problems?



GARGOYLE *Leather Oils & Greases*

SOCONY-VACUUM OIL COMPANY, INC., TANNERS DIVISION, 26 BROADWAY, NEW YORK 4, N. Y.

SPRUCE EXTRACT

POWDERED SUPER SPRUCE

LACTANX

■

Robeson Process Company

General Offices: 500 Fifth Avenue, New York, N. Y.

Operating Plant at Erie, Pa.

MECO EXTRACT

ONE GRADE—THE BEST

CHESTNUT WOOD EXTRACT

All Concentrations, Liquid to Dry Powder

Teas Extract Co.

6400 Centennial Boulevard

NASHVILLE 9, TENNESSEE

TENNESSEE PLANT
Nashville, Tenn.

ANDREWS PLANT
Andrews, N. C

1st CHOICE

for Higher Quality Leather Production

Better Grading Figures!
Better Cutting Figures!
Overall Economy!

Extracts — Pancreatic Bates — Fillers
Sole Leather Finishes - Tanners Sugar
Tanners Lime — Chemicals

L.H.LINCOLN & SON, INC.
COUDERSPORT, PA.

Tanak® MRX

MELAMINE RESIN TANNING AGENT

for upgrading both white and colored leathers

TANAK MRX Melamine Resin Tanning Agent is relied upon by experienced tanners to increase the desirable properties of today's leathers. Useful for upgrading both white and colored leathers, TANAK MRX gives increased grain tightness, increased weight, better "break", fuller bellies and flanks. It penetrates white leathers so thoroughly that maximum whiteness is retained even after deep buffing. You can count on TANAK MRX Melamine Resin Tanning Agent to increase the cutting value of your leathers.

Other performance-proved Cyanamid Tanning Specialties include:

DEPILIN® XC Unhairing Agent . . . for cleaner, whiter stock and better control;

CUTRILIN® Bates . . . the pancreatic "bates of choice" in the tanning industry;

TWECOTAN® Tanning Extracts . . . blends to meet specific tanning requirements;

DYEWOODS and **EXTRACTS*** . . a full line for every important need;

TANAK® Synthetic Tanning Agents . . . ideal for improving the quality of leather during both chrome and vegetable tanning;

BETASOL® OT Wetting Agent . . . most powerful wetting agent available for tanning.

Write today for complete information on any of these products

AMERICAN Cyanamid COMPANY

INDUSTRIAL CHEMICALS DIVISION

30 Rockefeller Plaza, New York 20, N. Y.

In Canada: North American Cyanamid Limited, Toronto and Montreal

*Made by Taylor White Extracting Company—Cyanamid sole distributors

VEGETABLE TANNERS

If you are interested in quality and customer satisfaction, you should investigate **ARKOTAN B.**

ARKOTAN B is a syntan that assists in the production of a smoother grain, improved tensile strength, fuller and rounder feel and a clear, even color.

ARKOTAN B assists in the solubility of your extracts, permitting greater penetration and better take-up and reduces the sludge in the bath when solid Quebracho is used.

ARKOTAN B when used in the color pit, wheel or tail liquors improves the appearance of the grain and maintains the correct acidity in the tail liquor without the addition of acid at this point.

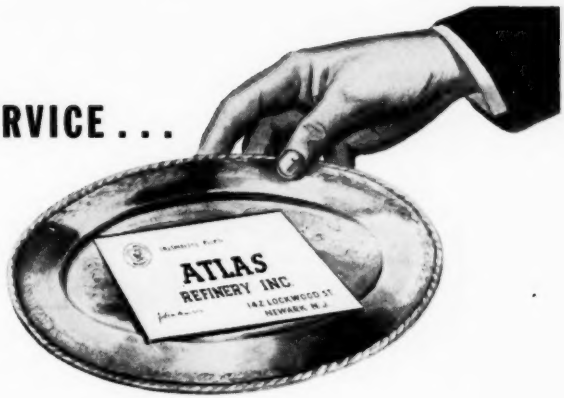
ARKOTAN B is used extensively in the re-tan wheels to produce added weight. Excellent for use on chrome re-tan upper leather where a tight break and solid feel is required.

Samples or demonstration of **ARKOTAN B** are available upon request.

ARKANSAS COMPANY, Inc.
Newark, N. J.

Manufacturers of Industrial Chemicals for over 50 years

AT YOUR SERVICE . . .



Let our *64 years* of specialized experience work for you . . . profitably

ATLAS

Guaranteed **OILS**

- **NEATSFOOT OILS**
- **SULPHONATED COD OILS**
- **SULPHONATED NEATSFOOT OILS**
- **SPLIT OILS**
- **MOELLONS, and many specialty Products**

ATLAS REFINERY SINCE 1867 QUALITY LEATHER OILS NEWARK, N.J.

A Name and Symbol
Pre-eminent in the Tannery Industry

• For over half a century, ATLAS has been a leader in the production of Quality Oils for the Tanning Industry, through extensive research to serve you better. ATLAS specialized research, plus many years of practical experience in the production of consistently high-quality, guaranteed oils is your assurance of uniformity to meet definite specifications. Give your leathers the "quality look" with ATLAS Oils.

ATLAS *Refinery, Inc.*

142 LOCKWOOD ST. NEWARK 5, N. J.

JACQUES WOLF

Chemicals

PRODUCE HIGH GRADE LEATHER

SYNEKTAN 0-230 **FAT LIQUOR L-90B**

For White Leather At Reasonable Cost
White Leather In Sheep, Goat, Calf Or Sides
White Tan In Combination With Chrome
White Nubuck, White Suede
White Bleached Chrome Stock
White Extract Type Of Leather

FUNGIZYME BATES
AS — BS — CS

Pancreatic bating salts of standard, controlled quality.

SULPHONATED OILS (Various Bases)

MONOPOLE OIL (For Finishing)

SAMPLES AND INFORMATION UPON REQUEST.

JACQUES WOLF & CO.
Chemicals PASSAIC, N. J.

Branches:
Carlstadt, N. J.
Los Angeles, Calif.

manufactured only for leather

excellent levelling power • excellent fastness to light, acid, alkali and fatliquor • good solubility.

IGENAL BROWNS

unsurpassed for chrome and vegetable tanned leather

IGENAL BROWN PGMA and PRMA . . . completely penetrate the leather . . . perfect levelling qualities.

IGENAL BROWN CRTA . . . surface dyeing . . . exceptional covering power.

IGENAL BROWN ITGA . . . partial penetration . . . particularly clear and bright when glazed.

Blended, these IGENALS produce a variety of brown shades.

Samples and technical information can be obtained from our home office or any of our branches.

GENERAL DYESTUFF CORPORATION

435 HUDSON STREET, NEW YORK 14, NEW YORK

BOSTON · CHARLOTTE · CHICAGO · PHILADELPHIA · PROVIDENCE · SAN FRANCISCO

OUR 155th YEAR

Natural Dyewood Products

Logwood

Fustic • Hypernic • Osage Orange

Produce level bottom shades for all colored leathers

•

Tanning Extracts

Dehydrated in the modern manner, perfect solubility, lowest cost

•

Coal Tar Dyestuffs, Synthetic Tans

•

NEW YORK COLOR & CHEMICAL CO. DIVISION

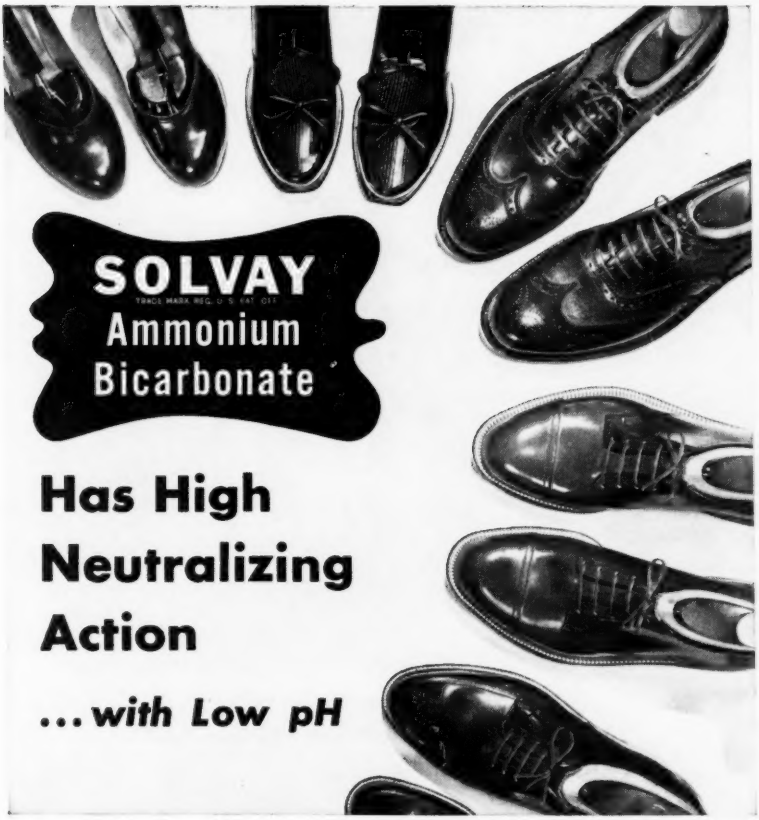
BELLEVILLE, NEW JERSEY

AMERICAN DYEWOOD CO.

374 MAIN STREET — BELLVILLE, N. J.

Factories:
CHESTER, PA. — BELLEVILLE, N. J.

Branch Offices:
BELLEVILLE, N. J. — DANVERS, MASS.
CHICAGO, ILL.
TORONTO, CANADA
MONTREAL, CANADA



SOLVAY AMMONIUM BICARBONATE penetrates the leather uniformly throughout the thickness of the hide; it helps improve the quality of your leathers by improving the grain and the dyeing characteristics. A 1% solution of SOLVAY AMMONIUM BICARBONATE has a pH of 7.8—ample proof that this quality product has a low pH while providing a high neutralizing value. For best results . . . for quality leathers . . . specify SOLVAY AMMONIUM BICARBONATE. Samples for testing purposes are available. Address your request to the nearest Solvay office.

SOLVAY PROCESS DIVISION
ALLIED CHEMICAL & DYE CORPORATION
61 Broadway, New York 6, N. Y.

BRANCH SALES OFFICES:

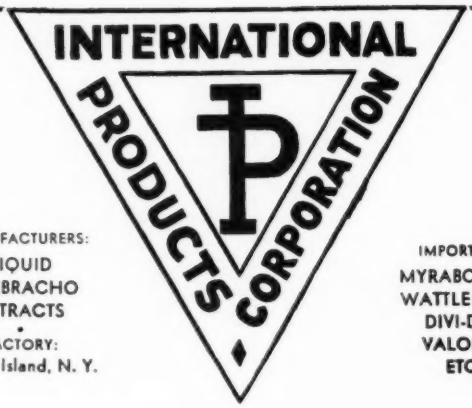
Boston • Charlotte • Chicago • Cincinnati • Cleveland • Detroit
Houston • New Orleans • New York • Philadelphia • Pittsburgh
St. Louis • Syracuse

SOLVAY

Other Solvay Products for Tanners

- CLEANSING SODA XX
- SNOWFLAKE* CRYSTALS

*REG. U. S. PAT. OFF.



MANUFACTURERS:
LIQUID
QUEBRACHO
EXTRACTS
•
FACTORY:
Staten Island, N. Y.

IMPORTERS:
MYRABOLAMS
WATTLE BARK
DIVI-DIVI
VALONIA
ETC.

INTERNATIONAL PRODUCTS CORPORATION

29 BROADWAY 6, NEW YORK

Representatives:

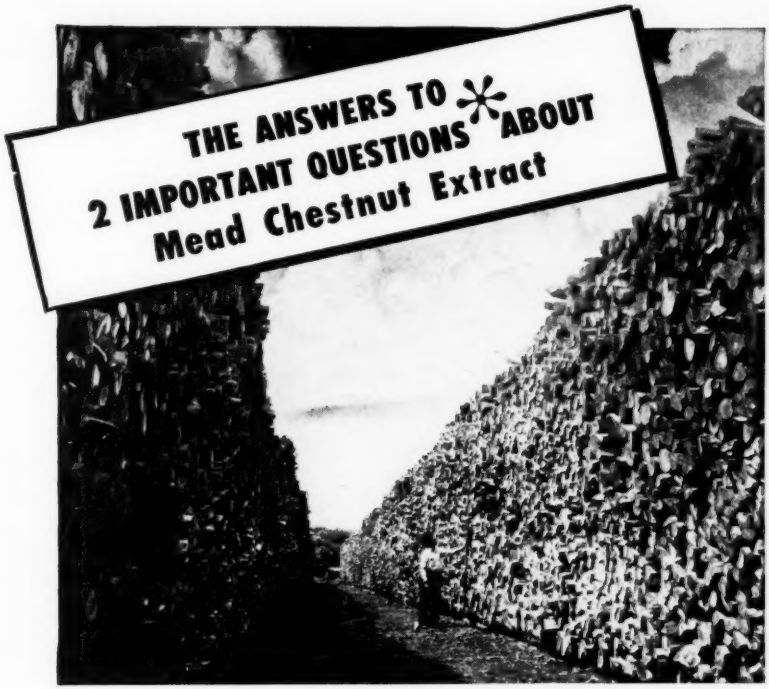
San Francisco - London, Canada - Boston
Havana, Cuba - Mexico City, Mexico

"SUPREMO"
BRAND
SOLID-ORDINARY

"LUNA"
BRAND
COLD WATER SOLUBLE

QUEBRACHO EXTRACTS

FACTORY AT PUERTO PINASCO, PARAGUAY



This is only a portion of the many stockpiles of chestnut logs that insure a continuous supply of Chestnut Extract.

1. Is the supply of Mead Chestnut Extract adequate?

Decidedly yes. Recent surveys show that there is enough chestnut wood in our forests to serve the leather industry for many years to come. Huge chestnut stockpiles, such as the one shown above, are converted under chemical control at five extract plants, insuring a steady supply of Mead Chestnut Extract.

2. Why is Mead Chestnut Extract preferred over other tanning agents?

Mead Chestnut Extract is a superior tanning material, made by America's largest producer of vegetable tanning extracts. Repeated experience has shown:

A. Chestnut tanned leathers do not oxidize, darken on exposure to light, or develop an uneven color on aging, as do leathers tanned with many other materials, vegetable or synthetic.

B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

Ask about Mead Cold Soluble Chestnut Extract for retanned leathers. And—for more pounds of plumper leather—standardize on Mead Chestnut Extract.

IT'S A FACT!

Mead Chestnut Extract will produce more pounds of plump leather per unit of tannin than any other tanning material.

Vegetable Tannin	Tan Yard Yield *(white weight basis)*
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

MEAD
CHESTNUT
EXTRACT

THE MEAD CORPORATION
Tannin Extract Division, Lynchburg, Virginia

QUEBRACHO EXTRACTS

SOLID	LIQUID	POWDERED
STANDARD	SM	"PUREX"
BRANDS	SMS	SMS

PLANTS: NEWARK, N. J. — PEABODY, MASS.

ALSO

Tanning Extracts and Raw Tanning Materials from all parts of the world.

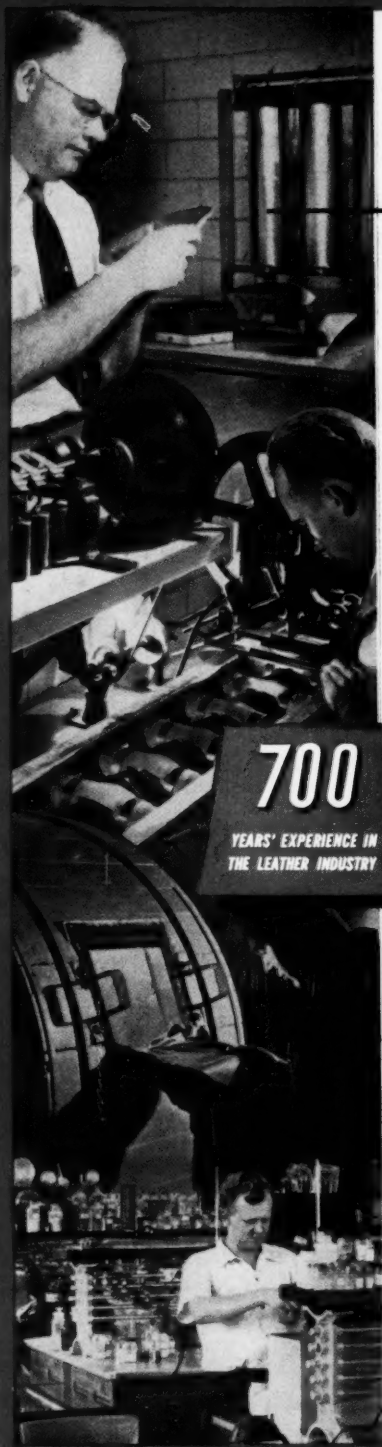
MYRABOLAMS	MANGROVE BARK
DIVI DIVI	VALONEA
TARA	SUMAC

WATTLE BARK
SOLID WATTLE EXTRACT
POWDERED MANGROVE and
VALONEA EXTRACTS

—IMPORTED BY—

THE RIVER PLATE CORPORATION

CHRYSLER BUILDING
405 LEXINGTON AVE., NEW YORK (17), N. Y.



Leather Chemicals with a Valuable Plus

Leather chemicals were the products that started this company in business 44 years ago. Today the bates, synthetic tanning materials, and finishes we are supplying to our customers are the best we have ever made. Our standard is dependable, uniform quality.

Our customers receive something else of measurable value—the benefit of more than 700 years aggregate experience of our leather research chemists and field staff. Every day in tanneries throughout the country Rohm & Haas representatives are applying knowledge of leather-making accumulated over more than 40 years. In addition they bring to bear on customers' problems the services not only of our leather laboratories but also other Rohm & Haas laboratories as well. Progressive tanners, year in and year out, continue to find these plus values helpful in the improvement of product quality.

Typical example of Rohm & Haas Leather Technology at work . . .

PRIMAL

Finishes for Upholstery Leather

PRIMAL resins are lastingly flexible. As components of water finish systems, they impart toughness as well as improved filling and leveling qualities. As a base coat for subsequent lacquer coatings, PRIMAL finishes give excellent adhesion and improved stability over a wide temperature range.

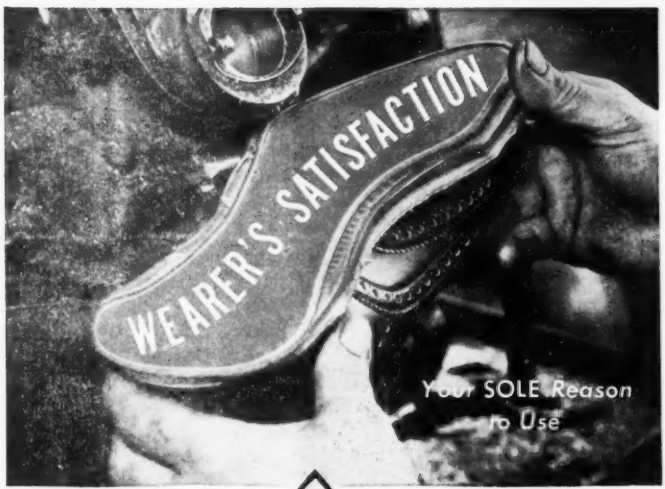
CHEMICALS FOR INDUSTRY

ROHM & HAAS COMPANY

WASHINGTON SQUARE, PHILADELPHIA 5, PA.

Representatives in principal foreign countries

PRIMAL *is a trademark, Reg. U. S. Pat. Off. and in principal foreign countries.*



DIAMOND A COMPOUND

TESTED and proved for 40 years—Diamond A is recognized as the Tanners' standard sponging and washing compound.

Here's why. Diamond A does a *double* job — (1) It prepares sole leather for rolling and protects the grain. (2) Used as a dip after rolling, it toughens the grain and improves color and finish.

Why delay? Let the Borne, Scrymser representative give you full particulars on Diamond A. You'll agree it's in a class by itself.

OTHER BORNE, SCRYMSER SPECIALTIES
(Get the Facts about These, Too!)
P COMPOUND for WHEELING
A COMPOUND for SPONGING
Supreme A Compound
Bretolene · Saxon Oil

BORNE SCRYMSER Since 1874
Our Laboratory Facilities are always at your disposal

BORNE, SCRYMSER COMPANY Elizabeth, N. J. Charlotte, N. C.

Save Hide Substance

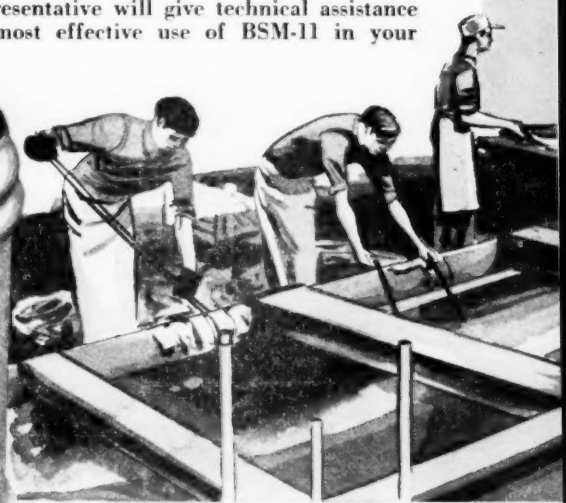
USE.. BSM-11 or BUTROL

as part of Good housekeeping practice

BSM-11 is highly effective in controlling the growth of microorganisms which digest hide substance during processing. BSM-11 is a liquid, thus easily added to the systems directly from the drums.

It has been demonstrated in many tanneries that the synergistic combination of bactericides and fungicides in BSM-11 provides efficient, economical control of bacteria, molds and yeasts which damage skins and hides.

Our representative will give technical assistance on the most effective use of BSM-11 in your process.



BUCKMAN
Laboratories, Inc.

Manufacturing Chemists • Memphis 8, Tennessee

Representatives in Most Countries

MICROORGANISM CONTROL SPECIALISTS

How HOOKER CHEMICALS help you cut processing costs

Hooker supplies you with:

- High-purity sodium sulfides that dissolve fast, for immediate use
- Caustic soda and other chemicals of consistent uniformity that help you standardize on processing methods

Make Hooker your source of supply. Write for delivery information and prices. Hooker Electrochemical Company, 3 Union St., Niagara Falls, N.Y.

Sodium Sulfide
Sodium Sulfhydrate
Sodium Tetrasulfide
Caustic Soda
Muriatic Acid
Sodium Benzoate
PARADI® (Hooker Paradichlorobenzene)

For precision control of unhairing solutions—Send for Hooker Bulletin 500. It tells how Hooker Sodium Sulfhydrate lets you adjust the sulfide and alkali strength of unhairing solutions exactly as you wish.

For time-saving data on soaking—Write for Hooker Bulletin 505. It describes how tanners are cutting soaking time in half by using Hooker Sodium Tetrasulfide solution.

HOOKER CHEMICALS

2-1634

From the Salt of the Earth

HOOKER ELECTROCHEMICAL COMPANY

NIAGARA FALLS TACOMA NEW YORK CHICAGO LOS ANGELES

CALAFENE
Binder and Filler

PIGMENT FINISHES Uniform quality binder, filler and carrying agent. Builds up body. Improves covering power and spread. Nourishes fiber and eliminates harsh feel. No manipulation necessary.

LEATHER FILLER Imparts permanent flexibility. Does not "pipe" or crack. Covers cuts and imperfections.

SUEDE SPLITS Plumps the skins, strengthens and builds up low ends. When sueded the skins have a velvety nap and full mellow feel. Does not lay on the surface.

APEX MARK of QUALITY

Established 1900
Apex Chemical Co., Inc.
225 West 34th St., New York 1, N. Y.

Manufacturers of a complete line of specialties for the tanning trade

UNION TANNERS SUGAR CHIPPED OR BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR
CHIPPED OR BILLETS UNION TANNERS SUGAR
NO NG
UN ETS
UN AR
CH GAR
NON-FOAMING UNIFORM CLEAR NON-FOAMING
UNION TANNERS SUGAR CHIPPED OR BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR

UNION STARCH & REFINING CO.
Established 1903
General Offices: COLUMBUS, INDIANA

THE PLANT BEHIND THE PRODUCT

Over 8½ acres of modern plant producing Tanning and Dyewood Extracts for the industry . . . Manufacturers of the famous CHEMBARK Natural Tanning Extracts for *Chemtan Co.* . Experienced technical advice furnished upon request.

TANNING AND DYEWOOD EXTRACTS

LOGWOOD • HEMATINE • FUSTIC
SUMAC • GAMBIER • HYPERNIC
WATTLE • QUEBRACHO • MYRABOLAM
DIVI-DIVI • TANNIC ACID

YOUNG EXTRACTS HAVE BEEN SERVING THE INDUSTRY FOR MORE THAN 84 YEARS

the **J. S. YOUNG CO.**

2701 Boston St., Baltimore 24, Md.
Philadelphia, Pa. • Chicago, Ill.
Paterson, N. J. • Danvers, Mass.

DEVELOPMENT AND

INTRODUCTION OF

BETTER **CHEM**ICALS FOR **TAN**NING

NARROW MOUTH, SCREW CAP

POLYETHYLENE BOTTLES

Flexible and unbreakable in normal use and highly resistant to chemical attack

2205-A.

BOTTLES, POLYETHYLENE, Narrow Mouth, Screw Cap. Polyethylene is a tough, lightweight, thermoplastic, paraffinic material with wax-like appearance and feel, possessing the following characteristics:

Flexible and unbreakable in normal use.

Unaffected by light.

Inert to water and ordinary buffer solutions.

Can be used at temperatures up to approximately 70° C.

Can be marked with usual glass marking wax pencils.

Not attacked significantly at room temperature by mercury, concentrated alkali, concentrated hydrofluoric, phosphoric, sulfuric, hydrochloric or chromic acids, dilute nitric acid, or hydrogen peroxide to 90%.

Specific gravity is 0.92.

However, they are **not** suitable for use with bromine, carbon bisulfide and concentrated nitric acid, or for prolonged storage of acetone, ether, xylene and other volatile organic substances. Polyethylene caps do not require liners and provide a seal which does not tend to "freeze" or slip.

2205-A. Bottles, Polyethylene, Narrow Mouth, Screw Cap, as above described, complete with polyethylene caps.

Capacity	2 oz.	4 oz.	8 oz.	16 oz.	32 oz.	½ gal.	1 gal.
Inside depth of cap, mm,	8	9	9	9	31	31	31
Each	**.22**	**.27**	**.41**	**.57**	**1.16**	**5.10**	**7.34**
Per dozen, one size only	**2.36**	**2.93**	**4.44**	**6.16**	**12.65**	**55.20**	**79.39**

NOTE—Also available, Polyethylene Caps only, for use with glass bottles; Bottles only, for use with either Polyethylene or moulded phenolic resin screw caps, and Fittings for conversion of above Bottles into Wash Bottles.

ARTHUR H. THOMAS COMPANY

Laboratory Apparatus and Reagents

WEST WASHINGTON SQUARE **PHILADELPHIA 5, PA.**

Teletype Services: Western Union WUX and Bell System PH-72

JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVIII JULY 1953 No. 7

DEAN WILLIAMS ..... *Editor*

EDITORIAL BOARD

H. B. MERRILL R. B. HOBBS F. O'FLAHERTY
R. E. PORTER J. H. HIGHBERGER H. G. TURLEY

Only such correspondence as pertains to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Correspondence in reference to subscriptions, advertising and other business should be addressed to the Secretary, Dept. of Leather Research, University of Cincinnati, Cincinnati 21, Ohio.

Checks for subscriptions and advertisements should be made payable to the American Leather Chemists Association.

Subscriptions—Members, $12.00 annually; Non-members, $15.00 annually.

Published monthly by the American Leather Chemists Association.

Entered as Second class Matter at the Post Office at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

Copyright, 1953, by the American Leather Chemists Association.

PAST PRESIDENTS OF THE A. L. C. A.

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VETCH, W. K. ALSOP, L. E. LEVI, C. R. OBERFELL, R. W. GRIFFITH, C. C. SMOOT, III, J. S. ROGERS, LLOYD BALDERSTON, J. A. WILSON, R. W. FREY, G. D. MCLAUGHLIN, FRED O'FLAHERTY, A. C. ORTHMANN, H. B. MERRILL, V. J. MLEJNEK, J. H. HIGHBERGER, DEAN WILLIAMS, T. F. OBERLANDER, A. H. WINHEIM, R. M. KOPPENHOEFER.

OFFICERS 1953-'54

President—H. G. Turley, 501 Camden Avenue
Moorestown, N. J.

President-Elect—E. S. Flinn, 1043 Ashland Place, Lynchburg, Va.

Secretary-Treasurer—Fred O'Flaherty, Department of Leather Research, University of Cincinnati, Cincinnati, Ohio.

Council

F. L. Collins, 6222 Notingham, **St. Louis 9, Mo.**

R. G. Henrich, Surpass Leather Company, 9th and Westmoreland Streets, Philadelphia 40, Pennsylvania.

C. A. Ross, The Ohio Leather Co., Girard, Ohio.

H. R. Wilson, B. D. Eisendrath, Memorial Laboratory, 702 Racine Street, Racine, Wisconsin.

J. R. Kanagy, Leather Division, National Bureau of Standards, Washington, D. C.

SECRETARY'S NOTICE

FOR SALE—One used evaporator-dryer for tannin analysis, 22 x 36 inches; good condition. Make offer. Box M2E, Dr. Fred O'Flaherty, University of Cincinnati, Cincinnati 21, Ohio.

The Chemistry of Vegetable Tannins

IX Quebracho

ROBERT C. PUTNAM and JOHN C. ROCKETT

United Shoe Machinery Corporation
Research Division
Beverly, Mass.

The optical rotation of purified quebracho tannin has not been previously reported. A sample of solvent purified extract (A) (1) containing one mole of water and a sample of calcium oxide purified extract (D) (1) containing three moles of water have been measured, and after correcting for the difference in water content, were found to give the same rotation.

An attempt was made to increase the methoxyl content of methylated quebracho by the use of dimethylaniline and dimethyl sulfate. Instead of increasing it, a reduction in the number of methoxyl groups from seven to six occurred. An effort to tosylate the methylated derivative with tosyl chloride in dimethylaniline likewise caused demethylation.

Quebracho extract (A) was tosylated directly. The product contained eight tosyl groups. This was treated next with nitric acid to produce an intermediate product which appeared to contain five tosyl groups and corresponded to the following formula:

$$C_{57}H_{42}NS_5O_{21}$$

$$\text{or } C_{22}H_{14}O_4\ (CH_3C_6H_4SO_2O)_5NO_2$$

By replacing the tosyloxy groups by hydroxyls and the nitro group by hydrogen, this basic formula is obtained:

$$C_{22}H_{20}O_9$$

Certain other degradation products have been obtained which also point to this formula.

Another set of degradation products has been discovered which indicates a slightly different basic structure. Quebracho extract has been degraded by fusion with mixed alkali to give a product which can be represented by the following:

$$C_{23}H_{20}O_8\text{-}0.5H_2O$$

By acetylation of this substance the following derivative was obtained:

$$C_{23}H_{13}O(O\ Ac)_7$$

By methylation the following was obtained:

$$C_{23}H_{16}O_4(OCH_3)_4$$

A methylated intermediate having the same analysis as the one directly above was prepared by first methylating quebracho and then fusing it with mixed alkali. Permanganate oxidation of this product gave veratric acid. This appears to indicate the presence of a second veratryl residue in the compound since such an oxidation of the original methylated quebracho also gave veratric acid. The foregoing set of products points to the following as a basic intermediate structure obtained in these degradations:

$$C_{23}H_{20}O_8$$

A mixed alkali fusion of quebracho gave B-resorcylic and protocatechuic acids. The former has not been previously found. It was identified by preparation of its bromo derivative.

Experimental

Rotation of Quebracho Extract

Substance A(1) $C_{31}H_{28}O_{11}.H_2O$

0.417% in water at 50°C

$\Delta = +0.23$

$$\left[\begin{matrix}\cdot\\ \alpha \\ \cdot\end{matrix}\right]^{50°C}_{D} = +55.1°$$

Substance D(1) $C_{31}H_{28}O_{11}.3H_2O$

0.417% in water at 50°C.

$\Delta = +0.25$

$$\left[\begin{matrix}\cdot\\ \alpha \\ \cdot\end{matrix}\right]^{50°C}_{D} = +55.7°\text{(corrected for larger water content)}$$

Loss of Methyl Group

One gram methylated quebracho was dissolved in five ml. warm dimethylaniline. Three ml. dimethyl sulfate was carefully added. After the reaction subsided it was warmed fifteen minutes on a water bath. After addition of dilute sulfuric acid and recovery of the precipitate it was dissolved in hot methanol, the insoluble portion removed, the solution chilled and the precipitate collected. Yield – 0.2 g. It did not melt but started to decompose at 160°C. It was alkali-soluble.

Calc.	$C_{31}H_{22}O_5(OCH_3)_6$			$.2H_2O$
	C63.8	H6.4	MeO(6)	26.7
Found	C64.0	H6.2	MeO	28.3
	64.0	6.1		28.4

Tosylation

Six grams of quebracho extract (A) was dissolved in 150 ml. pyridine and 28 grams p-toluenesulfonyl chloride was added. After standing overnight, it was dropped slowly with stirring into excess dilute sulfuric acid. After washing with water, the precipitate was immersed in methanol at room temperature, then collected on a filter. After redissolving in 50 ml. of pyridine, 7 grams, p-toluene sulfonyl chloride was added. After standing two hours, it was worked up as before. It was pinkish cream in color, weighed 15 grams and sintered at 112°C.

	Calc.	$C_{87}H_{76}O_{27}S_8$		
	or	$C_{31}H_{26}O_8(CH_3C_6H_4SO_2O)_8$		
	C 57.73	H4.23	S 14.17	
Found	C 57.99	H4.17	S 14.47	
	57.88	4.01	14.27	

Rotation Δ = +0.1 (0.17g in 15cc. acetone)

$$\left[\alpha\right]_D^{25^\circ} = +8.82^\circ$$

Nitration of the Tosyl Derivative

One gram of the tosyl compound was mixed with 20 ml. concentrated nitric acid and heated just below the boiling point for ten minutes. It was cooled, diluted with water and the yellow precipitate collected, washed with water, then methanol, dissolved in benzene at room temperature and poured into ligroin. It was cream-colored, weighed 0.6 g. and was found to decompose near 112°C.

	Calc.	$C_{57}H_{49}N\ S_8O_{21}$			
	or	$C_{22}H_{14}O_4\ \ (CH_3C_6H_4SO_2O)_5NO_2$			
	C 55.02	H 3.97	N 1.13	S 12.88	
Found	C 54.83	H 3.88	N 1.11	S 13.06	

Rotation Δ = +0.1° (0.10 g. in 9.8cc chloroform)

$$\left[\alpha\right]_D^{25.5^\circ} = +9.8^\circ$$

Formation of $C_{23}H_{20}O_8 \cdot 0.5H_2O$(M)

Ten grams of sodium hydroxide and ten grams of potassium hydroxide were heated in a dish until a clear melt was obtained. To this melt was added ten grams of quebracho (A) which had been thoroughly mixed with 15 g. of zinc dust. The addition was carried out slowly with efficient stirring. Heating of the mixture was continued for approximately ten minutes and the con-

tents then allowed to cool. Water was cautiously added and after the addition of 150 ml. the mixture was filtered through a sintered glass funnel to remove the zinc. The filtrate was cooled in an ice-water bath and acidified with hydrochloric acid. The acidified solution was thoroughly extracted with ethyl acetate, the ethyl acetate extract washed with water, dried over anhydrous magnesium sulfate, and evaporated to a viscous oily mass in vacuo. The oily substance was shaken with ether in which most of the substance dissolved. This ether extract was placed in a flask and upon adding benzene a light brownish precipitate was obtained which weighed 0.75 g. and melted at 146–148°C.

Calc.	$C_{23}H_{20}O_8 \cdot 0.5H_2O$	
	C63.7	H 4.9
Found	C63.7	H 4.7
	63.7	4.7

Acetylation of M

To a flask containing 10 ml. of acetic anhydride and 10 ml. of pyridine was added 0.2 g of substance M. The solution was warmed ten minutes on the steam bath and then allowed to stand two hours. It was added to a beaker containing 500 ml. of water. The acetyl derivative precipitated, yielding 0.25 g. of a light tan material of m.p. 130–132.5°. Upon dissolving the material in alcohol and treating with charcoal there was obtained upon cooling 0.14 g. of a white powdery product of m. p. 131–132.5°.

Calc.	$C_{23}H_{15}O(OAc)_7$		
	C61.83	H4.77	Ac 41.92
Found	C61.75	H4.82	Ac 41.15

Methylation of M

To a flask containing 50 ml. of ether was added 0.2 g. of product M followed by 20 ml. of ether containing ca. 0.7 g. of diazomethane. The solution was allowed to stand for five hours and then warmed gently on the steam bath to remove any excess diazomethane and finally reduced to dryness. The tan material obtained weighed 0.11 g. and melted at 162–164°.

Calc.	$C_{23}H_{16}O_4(OCH_3)_4$		
	C67.49	H5.87	MeO 25.83
Found	C67.54	H5.82	MeO 24.90

Formation of $C_{23}H_{16}O_4(OCH_3)_4(N)$

Two grams of methylated quebracho was fused with a mixture of four grams of sodium hydroxide and six grams of potassium hydroxide until brown. After treatment with water the insoluble portion was collected and washed with methanol and ether. It was dissolved in benzene, filtered and the product recovered from the filtrate. It weighed 0.85 g. and melted at 198–200°C.

Calc.	$C_{23}H_{18}O_4(OCH_3)_4$		
	C67.49	H5.87	MeO 25.83
Found	C67.47	H5.89	MeO 27.18
	67.35	5.80	27.35

Degradation of N

In a flask fitted with a condenser and dropping funnel was placed 0.28 g. of substance N, 1.0 g. of sodium hydroxide and 45 ml. of water. The mixture was heated by means of a water bath and a solution of 2.5 g. of potassium permanganate in 35 ml. of water was allowed to drop into the flask over a period of one hour. At the end of this time the mixture had only a slight purplish color due to an excess of permanganate. This excess permanganate was destroyed by the addition of a small amount of sodium bisulfite and the mixture then filtered to remove the manganese dioxide that had formed during the reaction. The filtrate, which had a slight yellowish color, was concentrated to a volume of approximately 30 ml., cooled, and acidified with hydrochloric acid. The acidified solution was extracted with ether, the ether extract was dried over anhydrous sodium sulfate and concentrated to a small volume. Upon cooling there was obtained a small amount (less than 20 mg.) of a solid which melted at 170–176°. It was crystallized from water and then melted at 180–181°. A mixed melting point with some authentic veratric acid showed no depression. Lack of material prevented the preparation of a derivative; however, an infra-red spectrogram showed it to be identical with veratric acid.

Isolation of Acids

Four grams of quebracho (A) (1) was heated with a mixture of 10 g. of sodium hydroxide, 10 g. of potassium hydroxide and 20 ml. of water. The temperature was not allowed to exceed 100°. After heating for twenty minutes the mixture was cooled, diluted with 100 ml. of water and acidified with hydrochloric acid. The acidified solution was thoroughly extracted with ether, the ether extract being dried over anhydrous sodium sulfate and distilled from a steam bath leaving a light brown material. This material was boiled for several minutes with 50 ml. of benzene. The benzene solution, which was light yellow in color, was separated from the insoluble material

and reduced in volume to approximately 20 ml. After standing for two days the benzene solution yielded 0.26 g. of crystalline material which melted at 102–110°C. A paper chromatogram procedure carried out according to directions (2) using butanol-acetic acid water in the ratio of 4:1:5 and spraying with 1.5% ferric chloride solution revealed the presence of two spots. A purplish colored spot had an R*f* of 0.91 and a greenish spot an R*f* of 0.84. Known samples of protocatechuic acid and B-resorcylic acid were run alongside the unkown mixture and found to have R*f* values of 0.84 and 0.91.

In order to prepare derivatives the mixture was separated by repeated fractional crystallization from water, the protocatechuic acid being the more soluble component. The B-resorcylic acid obtained weighed 0.08 g. and melted at 197–201°C. Its 5-bromo derivative was prepared according to directions (3) and melted at 206–208°C. A mixed melting point with an authentic sample of 2, 4-dihydroxy-5-bromobenzoic acid showed no depression.

	Calc.	$C_7H_5O_4Br$
	C 36.23	H 2.17
Found	C 36.16	H 2.05

The protocatechuic acid obtained melted at 194–197°C. and weighed 0.11 g. The 3,4-diacetyl derivative was prepared according to directions (4) and melted at 157–158°C. A mixed melting point with authentic 3,4-diacetoxybenzoic acid showed no depression.

Correction: In Article IV, Mangrove, of this series, J. Am. Leather Chemists' Assoc. **47**, 512 (1952), the formula for methylated mangrove was erroneously given. It should have read:

$$C_{20}\ H_{19}\ O_5\ (OCH_3)_7\ .2H_2O$$

$$\text{Rot.}\ \left[\ \alpha\ \right]^{25°C.}_{D} = +46.8°$$

$$C = 0.77\%\ \text{in acetone}$$

Bibliography

1. Putnam and Gensler, *J. Am. Leather Chemists' Assoc.* **46**, 613 (1951).
2. Bate-Smith and Westall, *Biochim et Biophys Acta* **4**, 427 (1950).
3. Sandin and McKee, *Org. Syntheses, Coll.* Vol. II 100 (1943).
4. Malkin and Nierenstein, *Ber.* **61**, 797 (1928).

Received February 2, 1953

Studies In Chrome Tanning*

XIX. Further Studies in the Neutralization of Chrome Tanned Leather

By EDWIN R. THEIS and W. R. LOTZ

From the Division of Leather Technology
Institute of Research
Lehigh University
Bethlehem, Pennsylvania
and the
Technical Laboratories of Albert Trostel and Sons Company
Milwaukee, Wisconsin

In a previous paper [1] the effect of neutralization, at various pH values' was shown on the shrinkage temperature and on the chromic oxide fixation of chrome tanned leathers. In this regard, it was postulated that neutralization at pH values greater than 5.0 did not bring about the formation of chromium hydroxide in the leather as might be expected. The shrinkage temperature of the leather did not decrease materially in the range pH 3.0 to 9.0 when sodium hydroxide, phosphate, and carbonate were used. The shrinkage temperature of the leather decreased at pH values greater than 7.0 when sodium bicarbonate, ammonium bicarbonate and borax were used as neutralization agents. These data were indicated rather strikingly in Figures 3 and 5 of the previous paper.

Studies were made relative to the layer-wise effect of the three neutralizing agents, sodium bicarbonate, ammonium bicarbonate, and borax. These data were not only of interest but were of some real practical value. The data substantiated much earlier work in that it was shown that the ammonium salt gave a much more thorough layer-wise neutralization than that obtained for sodium bicarbonate and borax.

In the earlier paper, older analytical methods, were used for the determination of protein bound acid and for leather basicity. Since, even today we have no real method for differentiating between the acid held by the protein and that associated with the chromium atom, the present writers used the Lehigh basicity method described elsewhere [2] for determining the over-all acid-base balance in the neutralized chrome tanned leather.

In order to evaluate further the leather produced through the use of certain neutralizing chemicals, certain of the test studies were repeated. The stock was taken in the "blue" after splitting and shaving. In all tests herein given, 100 pounds (shaved) of M weight stock were given a normal chrome retan and then, after washing, neutralized for coloring with the neutralizing chemicals as shown in Table I. All of the tests were mordanted with 2.0 per cent vegetable extract, colored, and fat liquored with an alkaline type of fat

*Presented before the Symposium on Tanning sponsored by the Tanners' Production Club of Wisconsin, 17 January, 1953.

liquor—pasted and then finished into 3.5 oz. weight smooth dress leather. In order to evaluate the effect of the neutralizing chemicals, each side was sampled and immediately after neutralizing split into layers on a Model A—U.S.M.C. splitting machine. These layers were then allowed to air dry and were used for the analytical data reported on later in this paper.

After staking and after finishing the sorting index, of the various test leathers, was determined as described in a previous paper [3].

Table I gives the test data taken at the time of neutralization.

TABLE I

Test No.	Neutralizing Material	pH Neutralization	Final pH
No. 1 – a	None	3.80	3.48
b	0.5% Borax	4.31	3.63
c	1.0% Borax	5.01	——
d	1.5% Borax	5.37	——
e	2.0% Borax	6.82	4.08
No. 2 – a	0.25% Bicarbonate*	4.61	3.82
b	0.5% Bicarbonate	5.18	3.80
c	1.0% Bicarbonate	6.10	——
d	0.1% NaOH	4.35	——
e	0.25% NaOH	5.32	3.90
No. 3 – a	1.0% Neutral Syntan**	4.00	3.60
b	0.5% Neutral Syntan**		
	0.5% Calcium formate	4.10	3.67
c	1.0% Neutral Syntan		
	0.5% Calcium formate	4.22	3.73
d	1.0% Neutral Syntan		
	1.0% Calcium formate	4.38	3.87
e	1.0% Neutral Syntan		
	0.5% Calcium formate	4.48	3.84
	0.5% Borax		

*Sodium bicarbonate
**Neutral Syntan of The Chemtan Company.

It will be noted from the various figures that over-all basicities of the leathers have been stressed.

Figure I shows data relative to the over-all basicities of the various leathers in the "blue". Figure I-A gives the data for sodium hydroxide neutralizing additions. These data indicate in a very striking manner the drastic neutralization of the grain layer (0.25 per cent sodium hydroxide equaling that for 0.5 per cent sodium bicarbonate and 1.5 per cent borax)—these data would be expected of such a strong alkali. It should be stressed, however, that the action of the strong alkali is confined almost entirely to the outermost layers of the chrome tanned stock.

Figure I-B shows data taken for sodium bicarbonate neutralization and here again the data indicate that the action is on the outer layers but not in such a drastic manner as for sodium hydroxide neutralization. As the amount of bicarbonate is increased, neutralization toward the center layers increases to some extent. This fact is especially indicated, for 1.0 per cent versus 0.5 per cent bicarbonate.

FIGURE I

SHOWING CHANGES IN OVER-ALL BASICITY USING DIFFERENT NEUTRALIZING AGENTS AND VARIOUS AMOUNTS OF SAME

SAMPLES TAKEN FOR LAYER-WISE SPLITTING IMMEDIATELY AFTER NEUTRALIZATION AND BEFORE COLORING

NEUTRALIZING AGENTS USED

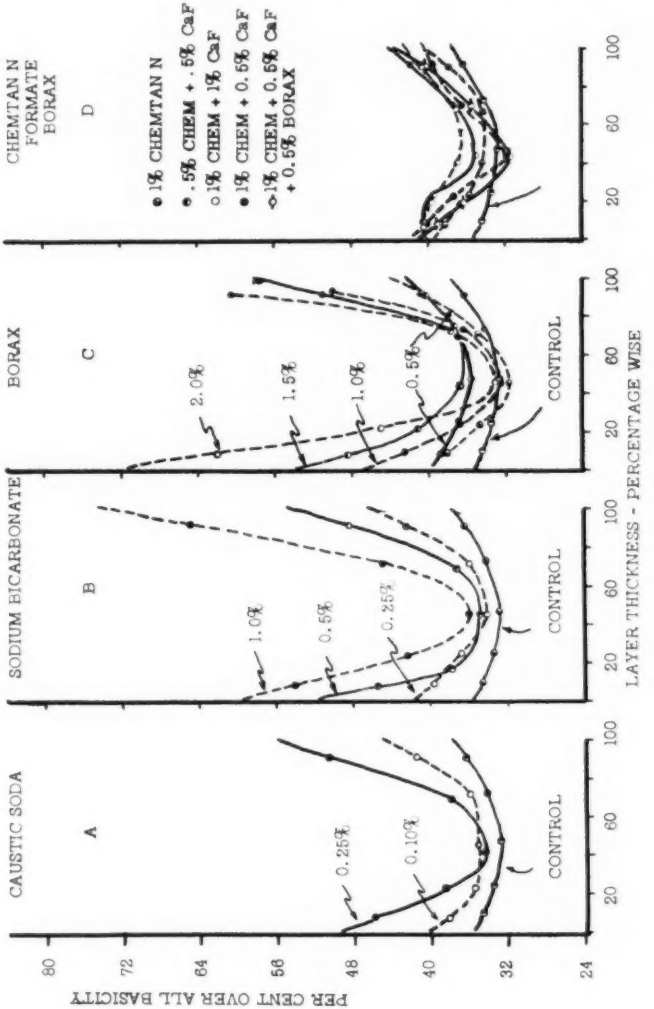


FIGURE II

NEUTRALIZATION USING SODIUM BICARBONATE

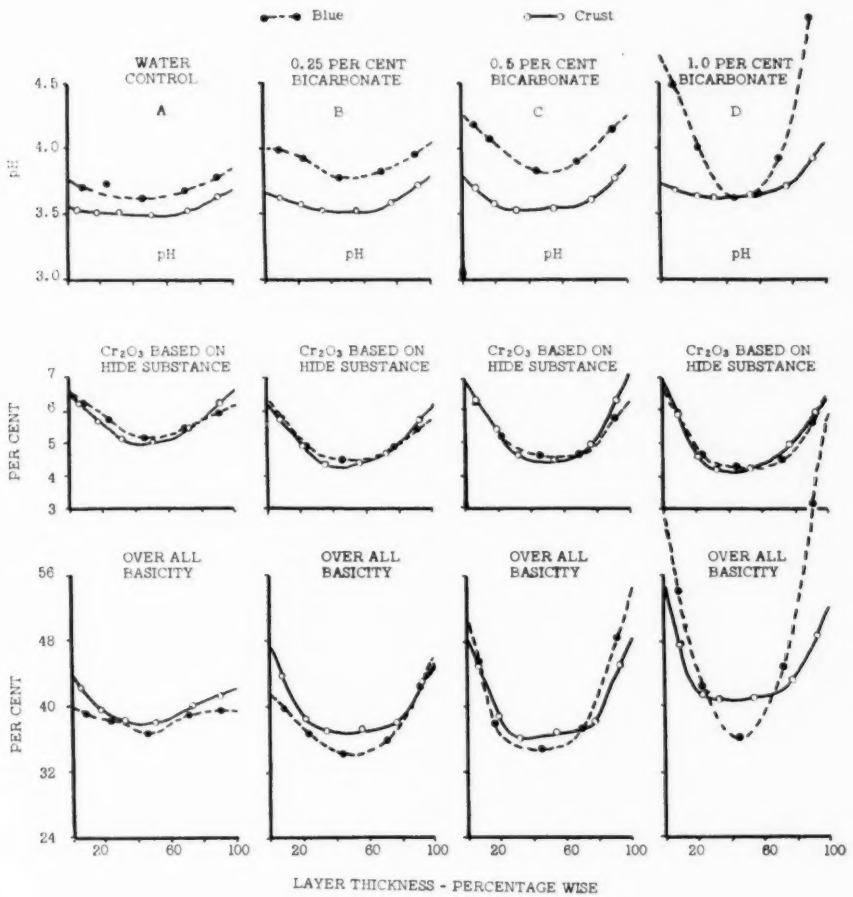


Figure I-C shows the neutralization effect of borax stratigraphically. With the exception of a lessened effect on the grain layer, as compared to an equivalent bicarbonate percentage, these data are similar to bicarbonate neutralization. There appears to be an even less penetrating effect when using borax.

Figure I-D gives data for a different type of neutralizing* chemical. Usually when we speak of neutralizing prior to the coloring and fat liquoring operation, we mean the addition of certain alkaline chemicals such as borax, sodium or ammonium bicarbonate, hypo (sodium thiosulfate), etc. Some leather manufacturers use neutral naphthalenic syntans as "setting" agents either alone or with mild alkalies for this particular operation. Thus Figure I-D indicates the action of neutral syntans, with and without mild alkali, on chrome tanned leather. As can be seen from the data the neutral syntan and especially the neutral syntan plus calcium formate increases the over-all basicity of the leather both on the grain layer and to some extent in the middle layers of the leather. This idea will be expanded upon later in this paper.

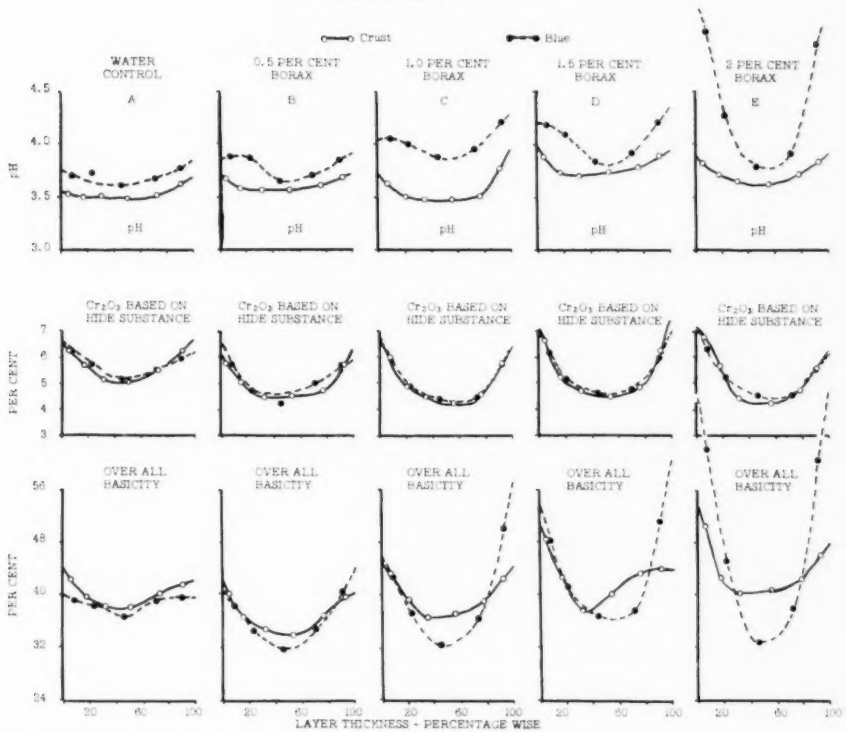
In general the majority of leather technologists use sodium bicarbonate or borax in this particular phase of neutralization. Figure II shows the effect of increasing additions of sodium bicarbonate during neutralization on the pH value, the Cr_2O_3 fixation, and the over-all basicity of the leather both in the "blue" and in the crust state. These data indicate: (1), the Cr_2O_3 fixed, as based on the hide substance value, is not materially changed by the operations subsequent to neutralization; (2) the Cr_2O_3 fixation is for all intents and purposes the same for all additions of bicarbonate—the decrease or increase of this factor being within experimental error; (3) the pH value of the grain and flesh layers is materially increased directly after neutralizing (dotted lines in Figure II) but is only slightly increased in the finished leather; the over-all basicity of the grain and flesh layers is materially increased directly after neutralization and this increase is carried over into the leather in the "crust". Careful study of the over-all basicity data shows that the basicity obtaining in the finished leather is greater than that for the leather just after neutralizing in the case of the control and the 0.25 per cent bicarbonate addition, but the basicity value of the grain and flesh layers, in the case of 0.5 per cent bicarbonate addition, is for all interests and purposes the same for the leather immediately after neutralization and in the finished state. However the basicity value obtaining for leather neutralized with 1.0 per cent bicarbonate is much greater in the grain and flesh layers, immediately after neutralization than that for the leather in the "crust". The data relative to the layer-wise pH value follow those of the over-all basicity values.

Figure III gives the data for the borax neutralization series, the additions of borax varying from zero to 2.0 per cent. Basically, with the exception of a milder action, the effect is similar to the sodium bicarbonate series as shown in Figure II. Again, it should be noted that small amounts of borax (0.5 per cent) appear to have little effect on the Cr_2O_3 fixation and not on the over-all basicity of the leather. With larger additions of borax, the over-all basicity

*This in tannery parlance may be known as "chrome setting" and is in reality a reduction in the total acidity of the system or a replacement of sulfato groups by other anions and is usually accompanied by an increase in over-all basicity of the entire system.

FIGURE III

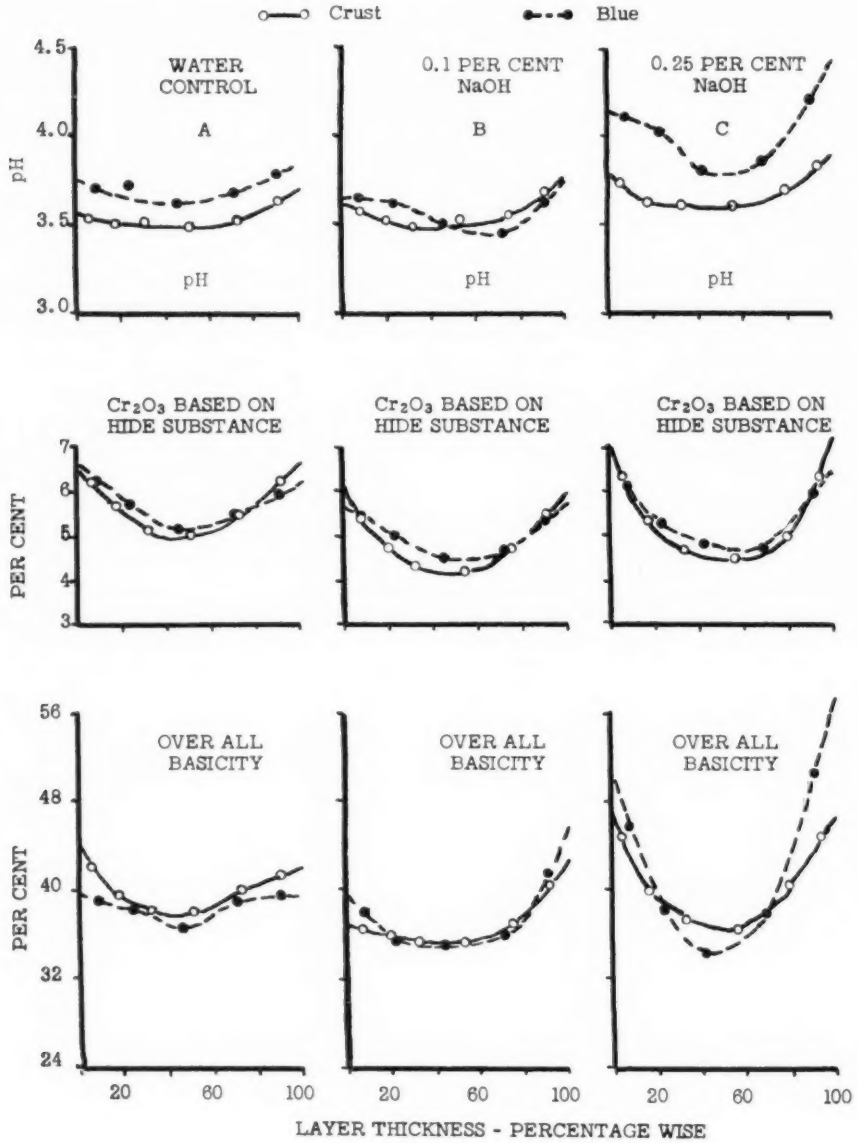
NEUTRALIZATION USING BORAX



and the pH value, are all increased to some extent while the Cr_2O_3 fixation remains essentially the same. It should be particularly noted, that when 2.0 per cent borax is used, the pH value and over-all basicity of the leather just after neutralization are considerably greater than for the leather in the "crust" state. Since this same condition obtains for the 1.0 per cent bicarbonate test, a possible explanation may be found in the process subsequent to the actual neutralizing process. The chrome tanned leather after neutralization was washed, dyed (acid being added for exhaustion purposes), washed, and then fat liquored with an alkaline type of fat liquor. Since the action of the alkali (either sodium bicarbonate or borax) is in the main on the grain and flesh layers of the skin, the washing, before and after coloring (together with the acid used in coloring for exhaustion) may remove any excess alkali present at that time in the grain layer—so as to decrease the over-all basicity and pH value of the leather. However, the large amount

FIGURE IV

NEUTRALIZATION USING SODIUM HYDROXIDE



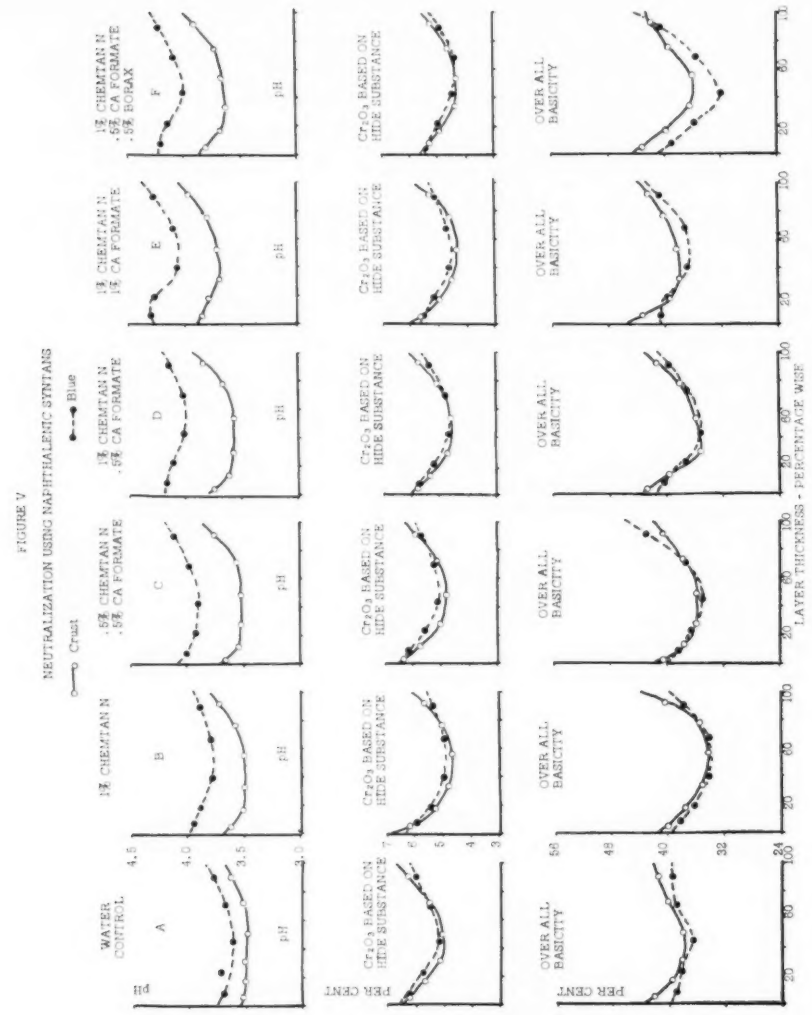
of alkali does increase the over-all basicity of the leather due to its reactivity with the basic chromium fixed with the protein of the skin. The alkaline fat liquor also plays a role in the over-all picture of the basicity figure as can readily be seen from the A, B, and C data of Figure II.

General tannery practice precludes the general use of caustic soda (sodium hydroxide) as a precoloring neutralizing agent. However, in these particular series of tests, small amounts of caustic soda were used in order to round out the general picture. Figure IV gives such data. As was the case for sodium bicarbonate and borax, a very small amount of caustic soda (0.1 per cent) gave: (1) an indication of decreased Cr_2O_3 fixation layer-wise especially in the center layers; (2), a slight change in over-all basicity; and (3), little change in the pH value of the leather. Using 0.25 per cent sodium hydroxide indicated: (1), an increase in Cr_2O_3 fixation in the outer layers; (2), a real increase in the over-all basicity of the outer layer with little change in the center layers of the leather; and (3), an increase in the layer-wise pH values of the leather. These data were similar to those given by the neutralization with 2.5 per cent borax or with 0.5 per cent bicarbonate.

Neutralizing chemicals such as sodium bicarbonate or borax act in general on the grain and flesh layers, with progressively less effect toward the center layer when large amounts of such reagents are used[2]. The conditioning of the split and shaved chrome tanned leather for coloring and fat liquoring may be brought about in another manner other than through the use of bicarbonate and borax—through the use of much milder reagents. Syntans of one type or another, mostly the acid or neutral naphthalenic types have been advocated as beneficial for coloring but not much has been written regarding their effect as "chrome setting" reagents* prior to the coloring and fat liquoring operations. The data shown in Figure V indicate the effects resulting through the use of a very mild neutral syntan with and without additional other mild alkalies. The data given for the neutral syntan alone (B portion of figure) show little or no effect on the layer-wise Cr_2O_3 fixation or the over-all basicity but some slight increase in the pH value of the grain and flesh layers. These data indicate rather strikingly that the use of neutral naphthalenic syntans can bring about a particular "conditioning for coloring" effect, without increasing the over-all basicity of the leather, that produces leather with a "sorting index" as good if not better than moderate amounts of borax. A study of the data given in Figure V shows the various neutralized effects caused by the naphthalenic syntan alone and in conjunction with formate and with formate and borax. These data demonstrate rather strikingly that the largest effect is on the pH value as compared with the control test.

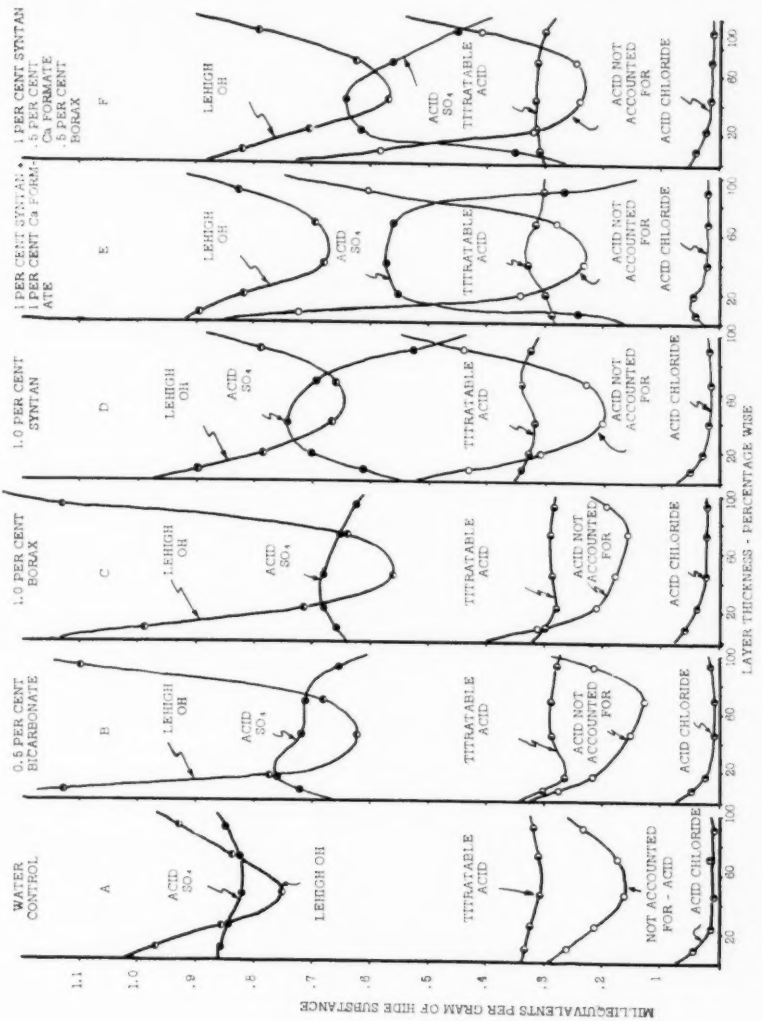
Figure VI gives data relative to the neutralizing effect of various reagents on the anion layer-wise distribution—compared with the control. Bicarbonate

*"Chrome setting" in this case is tannery terminology and means: (1), replacement of "sulfato" groups by the syntan anions; and (2) mild neutralization of some of the acid present in the system.



(0.5 per cent): (1), decreases the "sulfato" acidity especially in the other layers and to some degree in the middle layer; (2), increases the OH factor in the outer layers and decreases this factor in the middle layer; (3) does not affect materially the titratable acidity; and (4), increases the "acid not accounted for" in outer layers. One per cent borax shows: (1), that the "sulfato" groups are replaced to even a further degree than was the case for

FIGURE VI
THE EFFECT OF THE VARIOUS NEUTRALIZING AGENTS ON THE ANION LAYER-WISE DISTRIBUTION
SAMPLE TAKEN IMMEDIATELY AFTER NEUTRALIZATION



bicarbonate addition; (2), that the OH factor is decreased to about the same degree as with bicarbonate relative to the outer layers but to a greater degree in the center layer; (3), that the titratable acidity remains essentially the same; and (4), that the "non accounted for" acidity increases to a larger degree in the grain layer. These data are shown pictorially in Figure VI-A (control), VI-B, and VI-C.

Data for the syntan, with and without mild alkali neutralization, are shown graphically in Figures VI-D, VI-E, and VI-F. Thus for the syntan alone, the following comparisons can be made: (1), "sulfato" replacement is decidedly more marked (see VI-A) especially in the outer layers; (2), the OH factor existant in the outer layers is not as drastically affected as is the case for either bicarbonate or borax neutralization; (3), the titratable acid is not affected; and (4), the acid "not accounted for" is increased in the outer layers—due to the syntan and formed in the reaction.

FIGURE VII

DISTRIBUTION LAYER WISE OF VARIOUS CONSTITUENTS IN THE LEATHER CRUST STATE
(THREE DIFFERENT NEUTRALIZATIONS)

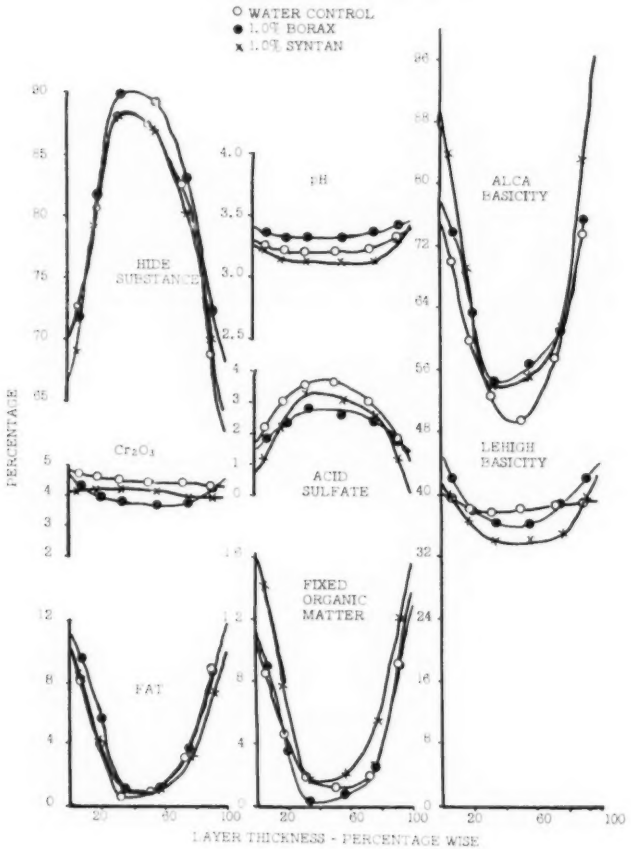


FIGURE VIII
THE SORTING INDEX OF THE VARIOUS TEST LEATHERS
IN THE "CRUST" AND "FINISHED" STATE

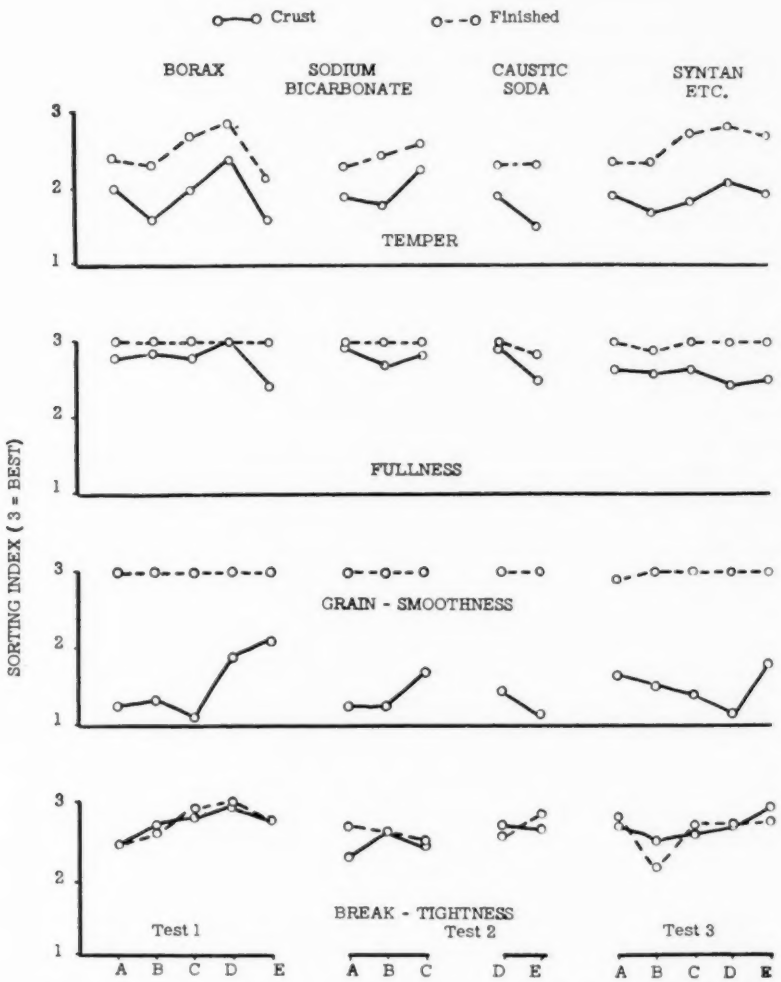


Figure VI-E and VI-F give data for syntan plus mild alkali neutralization. These data are similar to those given in VI-D with the exception that: (1), the "sulfato" acidity is still more markedly affected in all of the layers;

(2), the OH factor is reduced further; (3), the titratable acid remains the same; and (4), the acid "not accounted for" further increases in the outer layers. This last fact is due to the syntan anion replacing "sulfato" anions in the chromium complex fixed in the skin.

From data given in Figures V and VI, it might be stated that neutral naphthalenic syntans offer some useful and practical conclusions in that they can be used as neutralizing reagents alone or in conjunction with other mild alkalies for this purpose. More will be stated in this regard in future publications.

Figure VII shows the stratigraphs of the control, 1.0 per cent borax, and 1.0 per cent syntan neutralization. These data are of interest in that they show little difference with the exception of the fixed organic matter (fixed syntan) in the grain and flesh layers of the syntan treated leather. More will be stated relative to the use of syntan neutralization under sorting evaluation.

Figure VIII gives the sorting evaluation indexes for all the various neutralization test lots—both for the leather in the "crust" and finished condition. First, considering the leather both as "crust" and finished, it can readily be seen that; for the borax series Test 1-d (1.5 per cent) gives the best values for tightness, fullness, and temper; for the bicarbonate series Tests 2-b or c, give the best over-all picture with Test 2-c predominating; for the caustic soda series the sorting picture is poor, probably because of the high value of the leather over-all basicity on the grain layer; for the syntan series, the sorting picture is very good, especially Tests 3-c and d (syntan plus formate). A careful study of Figure 8 will be of more than worth while interest especially if these data are correlated with the chemical data given in previous portions of this paper.

Summary

In the neutralizing paper published in 1951, we had postulated from data, relative to pH value, Cr_2O_3 content, and shrinkage temperature, that at pH values greater than 5.0 the chromium complex fixed on the skin might have changed from a cationic type to an anionic or possibly even a non-ionic type. We had further demonstrated that sodium bicarbonate and borax neutralization affected only the grain and flesh layer whereas ammonium bicarbonate gave a much more thorough neutralization through its greater layerwise penetration.

In the present studies, the authors have used the Lehigh over-all leather basicity method for demonstrating the neutralizing effect and activity of the neutralizing agents. This method gives a truer picture relative to the differences obtaining when one or another of the neutralizing agents are used.

The present studies re-emphasize the findings in the earlier work and point out additional facts; (1) all of the neutralizing agents have a definite effect

on the grain layer; (2) all reduce the sulfato acidity of the grain layer; (3) alkalies such as bicarbonate, borax, or caustic soda reduce the sulfato acidity and increase the over-all basicity of the grain layer by a direct neutralizing action, while the very mild neutral naphthalenic syntan replaces the sulfato acidity but affects but slightly the over-all basicity of the leather (compare 1 per cent borax, 1 per cent bicarbonate with 1 per cent syntan).

The use of mixtures of syntan and calcium formate as neutralizing agents indicate some interesting practical trends, especially the mixture of 1 per cent neutral syntan and 1 per cent calcium formate. The data given in Figure VI-E show that the over-all basicity (as measured by the Lehigh OH data) is but little affected by the additional formate but the acid sulfate in the grain layer is reduced drastically. The sorting evaluation index for this test, (Figure VIII, Test 3-D), is one of the best of evaluation tests made in this series.

Figure VII again emphasizes the error in the ALCA leather basicity method which is not present in the Lehigh over-all basicity measurement. This is especially true for leathers in the "blue" which have been treated with syntans or for finished leather. The ALCA method would seem to indicate that most of the chromium present is of very high basicity while the new method gives expected values.

Neutralization prior to coloring and fat liquoring has always been considered a very important and necessary operation. Too little attention has been given to this process in the past. We know that the kind of neutralizing alkali used; the time period of neutralization, the temperature and washing are all of importance. We further know from practical experience that coloring must immediately follow neutralization due to the fact that the usual type of neutralizing affects only the grain and flesh layers and if much time elapses prior to coloring there will be bleeding of acid outward from the center layers to the grain and flesh layers. The usual practice of employing such alkalies as sodium bicarbonate or borax causes a sharp increase in over-all basicity of the grain layer but does not materially change the center layers of the skin. The present authors believe that if the neutralization should be such as to give practically the same over-all basicity layer wise, it would tend to give a better leather relative to tightness, crackiness, etc., in the finished leather. Such a tendency is indicated by the use of neutral naphthalenic syntans either alone but preferably in the presence of formate. A careful study of Figures II-C and D, III-C, V, VI-D and E, and VIII will give information of some practical value.

The investigations relative to neutralization prior to coloring are being continued in a cooperative manner between the plant and the laboratory and will be reported on in a later paper in this series. The use of calcium formate with and without neutral syntan have already shown some very interesting trends—since the use of calcium formate as a partial neutralizing

agent changes the free sulfuric acid to formic acid and thus rids the skin of the strong mineral acid. In addition the formate anion replaces the sulfato anion and thus gives a different chrome complex in the grain and flesh layers. If calcium formate and neutral syntan are used (1 per cent formate and 1 per cent syntan) additional replacement of sulfato groups take place while the over-all basicity of the leather is but little affected.

Acknowledgment

The writers take great pleasure in thanking the American Cyanamid Company, the Diamond Alkali Company, and the Mutual Chemical Company of America together with the Albert Trostel and Sons Company for the grants in aid, without which this development could not have been prosecuted.

Bibliography

1. Theis, E. R., Nayudamma, Y., and Kritzinger, C. C., *Amer. Lea. Chem. Asso.* **46,** 220, (1951).
2. Thorstensen, T. C., and Theis, E. R., *ibid.*, **47,** 588, (1952) and further unpublished data.
3. Theis, E. R., and Lotz, W. R., *ibid.*, **47,** 219, (1952).

Received, February 3, 1953.

Studies In Chrome Tanning*

XX Further Studies in the Use of Syntan in Chrome Tanning

By W. R. Lotz and Edwin R. Theis

From the Division of Leather Technology
Institute of Research
Lehigh University
Bethlehem, Pennsylvania
and the
Technical Laboratories of the Albert Trostel and Sons Company
Milwaukee, Wisconsin

In a previous paper[1] the writers made a careful and rather comprehensive investigation relative to the use of acid and neutral naphthalenic syntans as adjuncts in the chrome tanning operation. It was found that, whether the syntans were used in the pickle or in the chrome liquor, the syntan affects the chromium salt fixed and in general decreased the Cr_2O_3 fixed in the grain layer of the skin. This was found to be especially true in non-formato type tannage. If formate was present during the chrome tannage the presence of syntans exerted a beneficial effect in that the Cr_2O_3 fixed layer-wise in the

*Presented before the Symposium on Tanning sponsored by the Tanners' Production Club of Wisconsin, 17 January 1953.

TABLE I

The Combined Bate-Pickle Tan Processes Used

Non-Formato-Chrome Tannage		Formato-Chrome Tannage	
Stock—200 lbs. white weight*		Stock—200 lbs. white weight	
Wash 20 minutes at 90° F.		Wash 20 minutes at 90° F.	
Drain		Drain	
Float 20 gals. water at 90°F.		Float 20 gals. water at 90°F.	
Acid Wash: 0.33% sulfuric acid		Acid Wash: 0.33% sulfuric acid	
1 gal. cold water	5 min	1 gal. cold water	5 min
Add: 0.08% Hydrated Lime (in water suspension)	5 min	Add: 0.08% Hydrated Lime (in water suspension)	5 min
Bate: 1% Bate (pancreatic)	1 hour	Bate: 1% Bate (pancreatic)	1 hour
Wash 15 minutes at 65–70° F.		Wash 15 minutes at 65–70° F.	
Drain		Drain	
Float 10 gals. water at 70° F.		Float 10 gals. water at 70° F.	
Pickle: 4½% salt	5 min	Pickle: 4½% salt	5 min
Add: 1¾% sulfuric acid		Add: 2% sodium formate (dry)	Start Drum
2 gals. cold water	60 min	Add: 1¾% sulfuric acid	
Tan**: 1¼ gals. 40% basic chrome liquor (with or without dissolved syntan or replacement tanning material)	2½ hours	2 gals. cold water	60 min
		Tan**: 2¼ gals. 40% basic chrome liquor (with or without dissolved syntan or replacement tanning material)	44 2½ hours
Add: Bicarbonate of soda (and/or syntan)	3 feeds	Add: Bicarbonate of soda (and/or syntan)	3 feeds
3 gals. water at 90°F.	30/30/40 min.	3 gals. water at 90°F	30/30/30 min.
Add: Disinfectant	30 min.	Add: Disinfectant	30 min.
Pull and Pile***		Pull and Pile***	

*Stock: 200 lbs. white weight per test—out of 43–50 lb. hides of city butcher quality. Beam house process includes 1 day soak and 2 day unhairing.

**Chrome: 40% basicity sugar reduced liquor; 15% Cr_2O_3; aged for one week after reduction; syntans or other materials added just before using. RPM of drums = 17.

***Color and Fat: Stock split in "blue" for 3 to 3½ oz. finished smooth dress leather; chrome retanned; 2% extract mordant; no syntan or replacement tanning material; alkaline fat-liquor.

skin was practically uniform. It was also found that the syntan anion replaced "sulfato" ones in the chromium salt fixed and thus a different type of chromium salt was fixed upon the skin fibers of the grain layer. The presence of syntan appeared to redistribute the natural fat in the skin while the presence of formates appeared to stabilize the syntan-chromium salt and actually gave a superior leather. The presence of formates during the syntan-chrome tannage not only stabilized the Cr_2O_3 fixation but also that of the pH value and the over-all basicity of the leather.

In all of the previous series of syntan studies, the syntan had been added to either the pickle or to the chrome liquor just prior to its use in the chrome

tannage. In order to further our knowledge of the syntan-chrome tannage, it appeared desirable to investigate the effect of aging on the syntan-chrome liquor system. This aging effect was accomplished in two ways: (1) adding the neutral syntan to the chrome liquor, heating to 180° F. holding this temperature for one hour, and then allowing the liquor to cool; and (2) adding the required amount of neutral syntan to the chrome liquor and then allowing the mixture to age for one week at ordinary temperatures.

The experimental procedure used for the following series of tests is identical to that already described elsewhere[1] but the following Table gives the combined Bate-Pickle-Tan procedure used for both the non-formate and the formate process.

For the analytical data herein shown, each side was sampled, first, after splitting and shaving; and secondly in the "crust". The samples taken were 3 inch by 3 inch squares, which were in turn split into 7 to 8 layers. The chemical data taken were identical to that specified in the previous paper. In addition to the chemical data, careful sorting of the test lots of leather was made in the "crust" and finished condition.

1—Effect of Addition of Neutral Syntan during Chrome Tannage. Series U—The Effect of Aging When Using A Neutral Syntan as an Adjunct during Chrome Tannage

For these studies the neutral syntan was used in conjunction with 40 per cent basic sugar reduced chrome liquor. In all cases 200 pounds "white

TABLE II

Showing Variations in the U-Series

Test No.	Formate	Syntan	Neutalization
1 (Control)	2%	None	34 oz. $NaHCO_3$
2	2%	(a) 0.5% Neutral	32 oz. "
3	2%	(a) 1.0% "	32 oz. "
4	2%	(a) 2.0% "	30 oz. "
5	2%	(a) 5.0% "	32 oz. "
6	2%	(b) 0.5% "	36 oz. "
7	2%	(b) 1.0% "	34 oz. "
8	2%	(b) 2.0% "	33 oz. "
9	2%	(b) 5.0% "	26 oz. "
10	None	(b) 0.5% "	26 oz. "
11	None	(b) 1.0% "	27 oz. "
12	None	(b) 2.0% "	25 oz. "
13	None	(b) 5.0% "	24 oz. "

Neutral Syntan—Tamol N (Rohm and Haas)

(a) Add the required amount of Tamol N to just the right amount of the chrome liquor. Heat to 180°F and keep at this temperature for one hour. Allow to cool; then add to drum as in regular tannage.

(b) Add required amount of Tamol N to the chrome liquor. *Do Not Heat*, but allow to age for one week and then add this liquor to the drum.

weight" stock was tanned with the various prepared chrome tanning liquors. The blue stock, after splitting and shaving was colored and fat liquored and made into M (3.5 ounce) weight smooth dress leather. Some 13 different test lots were made, the particulars of which are given in Table II.

The control data, taken during the combined Bate-Pickle-Tan process, are given in Table III.

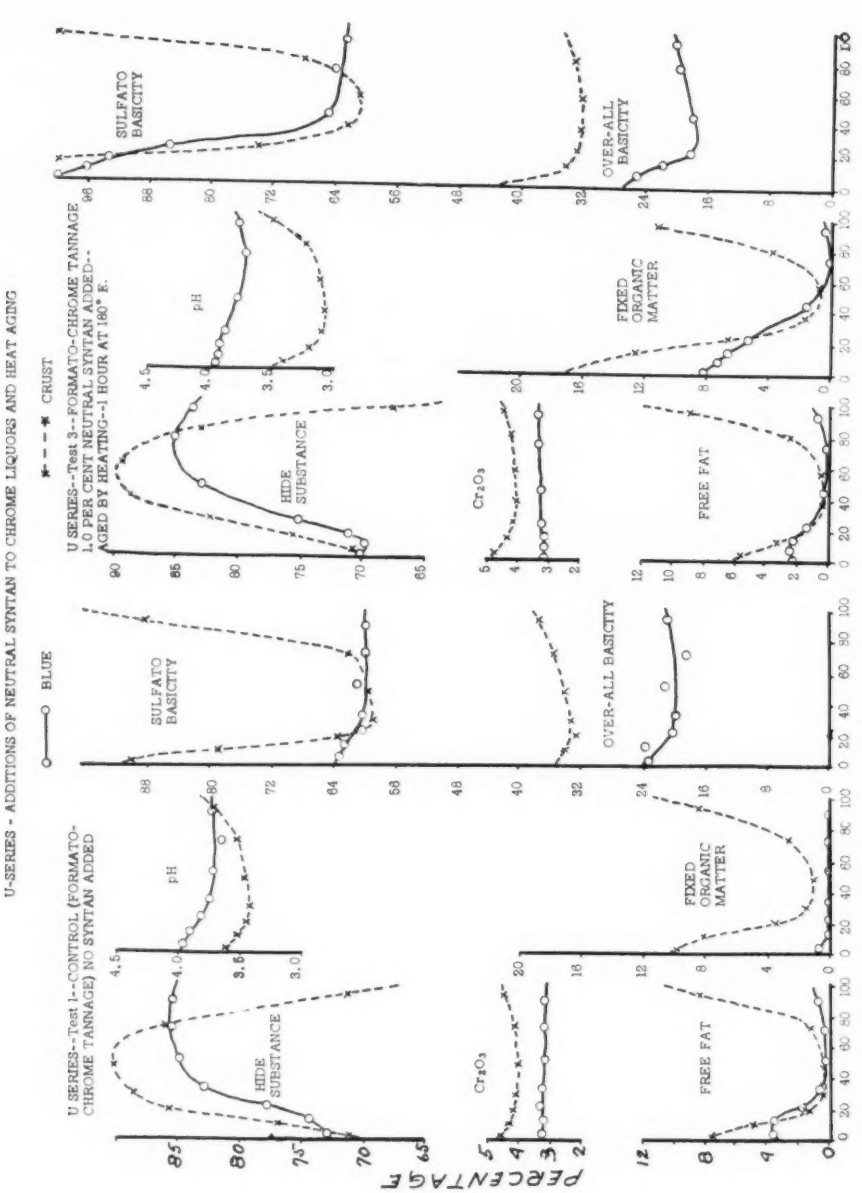
TABLE III

Test No.	pH of Chrome Liquor as Used	After Bate	After Pickle	After Tan	After Neut.	Shrink Temp °C.
1	2.52	8.58	3.40	3.08	3.82	102
2	2.60	8.68	3.38	3.08	3.82	107
3	2.57	8.63	3.40	3.13	3.92	104
4	2.54	8.69	3.47	3.22	3.97	103
5	2.63	8.68	3.40	3.13	3.88	97
6	2.62	8.56	3.41	3.28	3.90	103.5
7	2.60	8.58	3.50	3.34	3.91	102.5
8	2.61	8.63	3.49	3.37	3.90	99.5
9	2.70	8.62	3.66	3.60	4.00	98
10	2.70	8.58	1.33	2.05	3.10	83.5
11	2.60	8.53	1.27	1.95	3.10	82.5
12	2.60	8.58	1.32	2.09	3.12	81.5
13	2.67	8.50	1.32	2.17	3.17	81.

Tests 1, 2, 3, 4, and 5 of Series U consistitute a partial series of tests in which the neutral naphthalenic syntan was added to the chrome liquor and then the mixture heated for one hour at 180° F. After cooling this new liquor was used for the chrome tannage. A careful study of the chemical data in the several stratigraphic charts—Figure I will be of some practical interest since all of these tests were of the formato-chrome tannage type and the neutral syntan varied from 0 to 5 per cent. The Cr_2O_3 layer-wise distribution is practically a straight line function, again substantiating results obtained in previous studies. However, when the neutral naphthalenic syntan is added to the chrome liquor and then the mixture heated, this chrome liquor does not cause the drastic decrease in Cr_2O_3 fixation as was found when the same syntan was merely added to the chrome liquor prior to tannage. In this partial series, we find that the Cr_2O_3 fixation decreases from approximately 3.25 per cent for no syntan added to 2.9 per cent when 5.0 per cent neutral syntan had been used. Actually, it appears as though the addition of 0.5 per cent syntan increased the Cr_2O_3 fixation from 3.25 to 3.5 per cent—an actual advantage. This same advantage is also demonstrated by the increased shrinkage temperature of the leather produced in this particular test. The

FIGURE I

U-SERIES - ADDITIONS OF NEUTRAL SYNTAN TO CHROME LIQUORS AND HEAT AGING



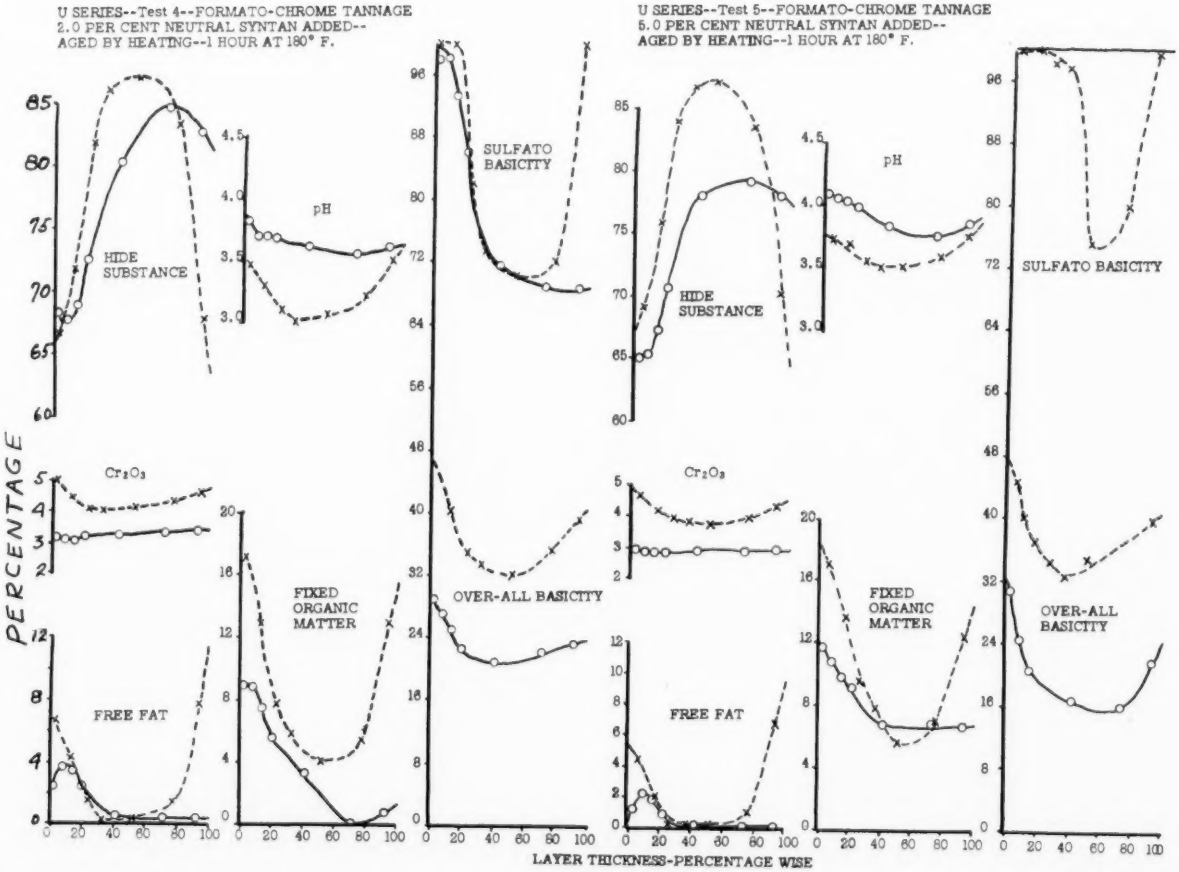
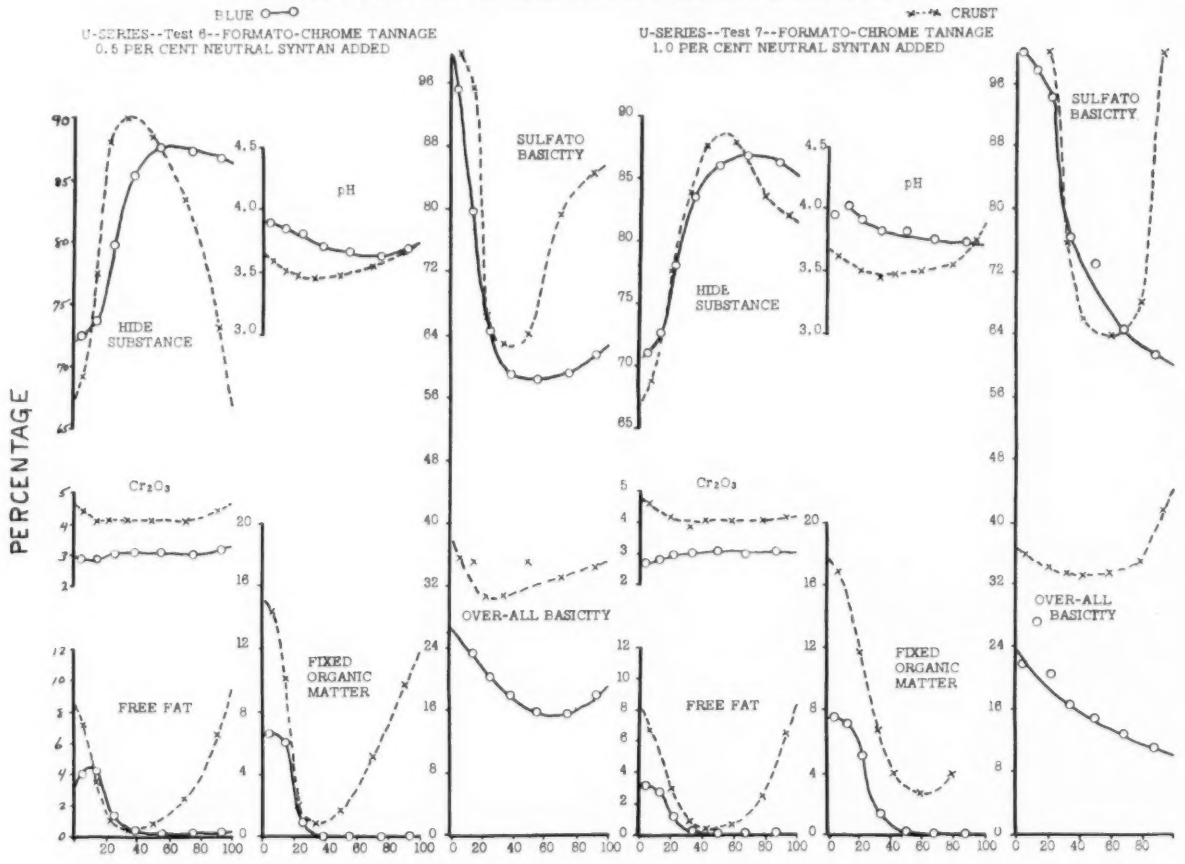
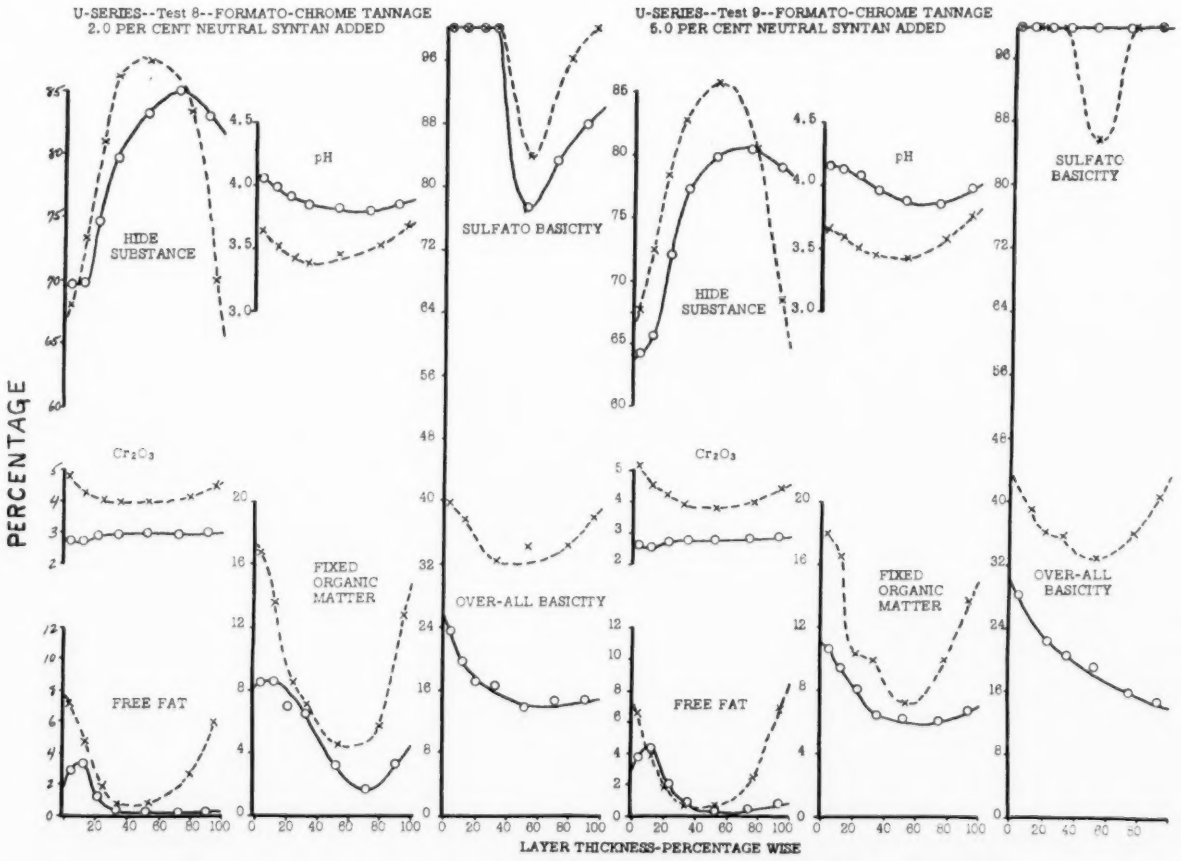

U SERIES--Test 4--FORMATO-CHROME TANNAGE
2.0 PER CENT NEUTRAL SYNTAN ADDED--
AGED BY HEATING--1 HOUR AT 180° F.
U SERIES--Test 5--FORMATO-CHROME TANNAGE
5.0 PER CENT NEUTRAL SYNTAN ADDED--
AGED BY HEATING--1 HOUR AT 180° F.
PERCENTAGE
HIDE SUBSTANCE
pH
SULFATO BASICITY
Cr_2O_3
FIXED ORGANIC MATTER
OVER-ALL BASICITY
FREE FAT
LAYER THICKNESS-PERCENTAGE WISE

FIGURE II
U-SERIES-ADDITIONS OF NEUTRAL SYNTAN TO CHROME LIQUOR AND AGED COLD ONE WEEK




U-SERIES--Test 8--FORMATO-CHROME TANNAGE
2.0 PER CENT NEUTRAL SYNTAN ADDED
U-SERIES--Test 9--FORMATO-CHROME TANNAGE
5.0 PER CENT NEUTRAL SYNTAN ADDED
PERCENTAGE
HIDE SUBSTANCE
pH
SULFATO BASICITY
Cr_2O_3
FIXED ORGANIC MATTER
OVER-ALL BASICITY
FREE FAT
LAYER THICKNESS-PERCENTAGE WISE

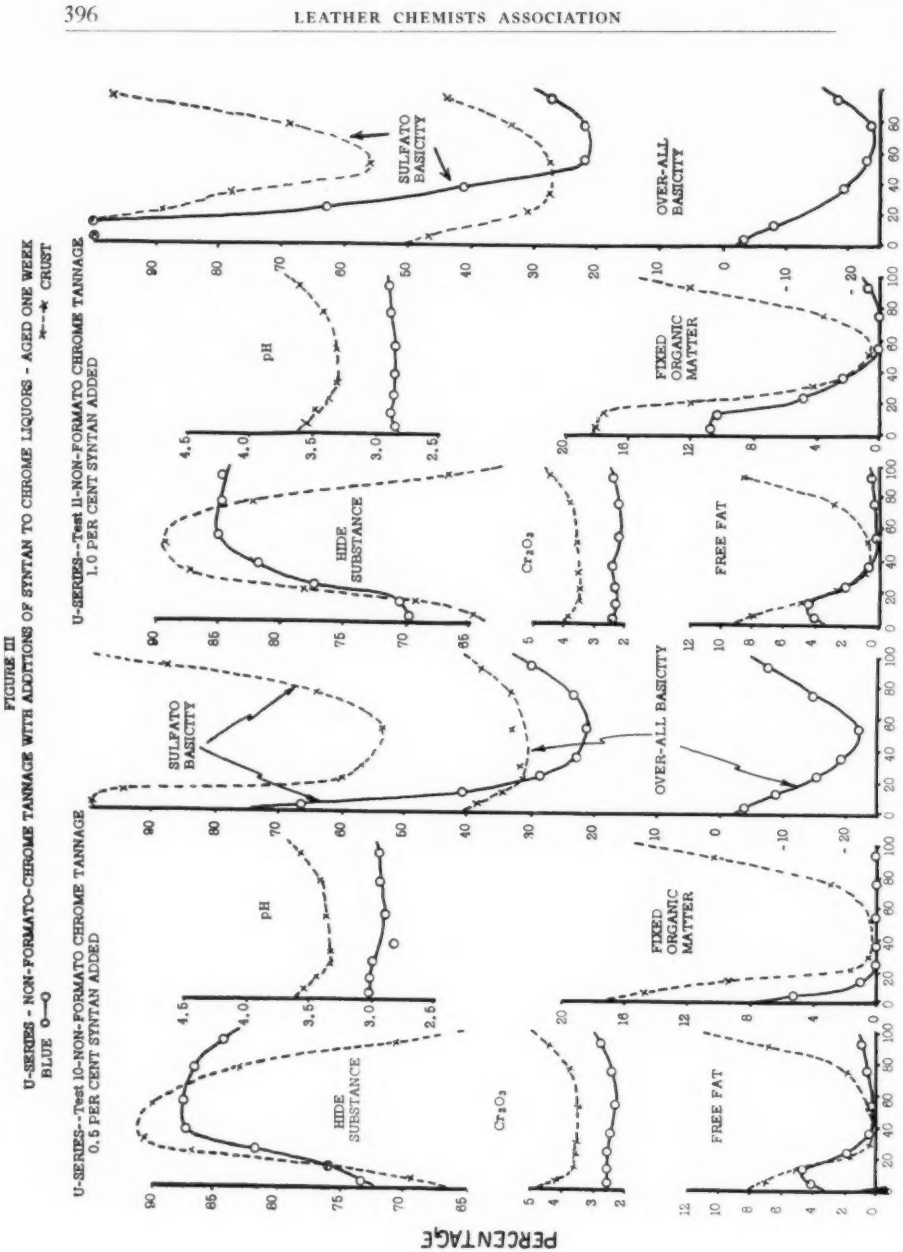
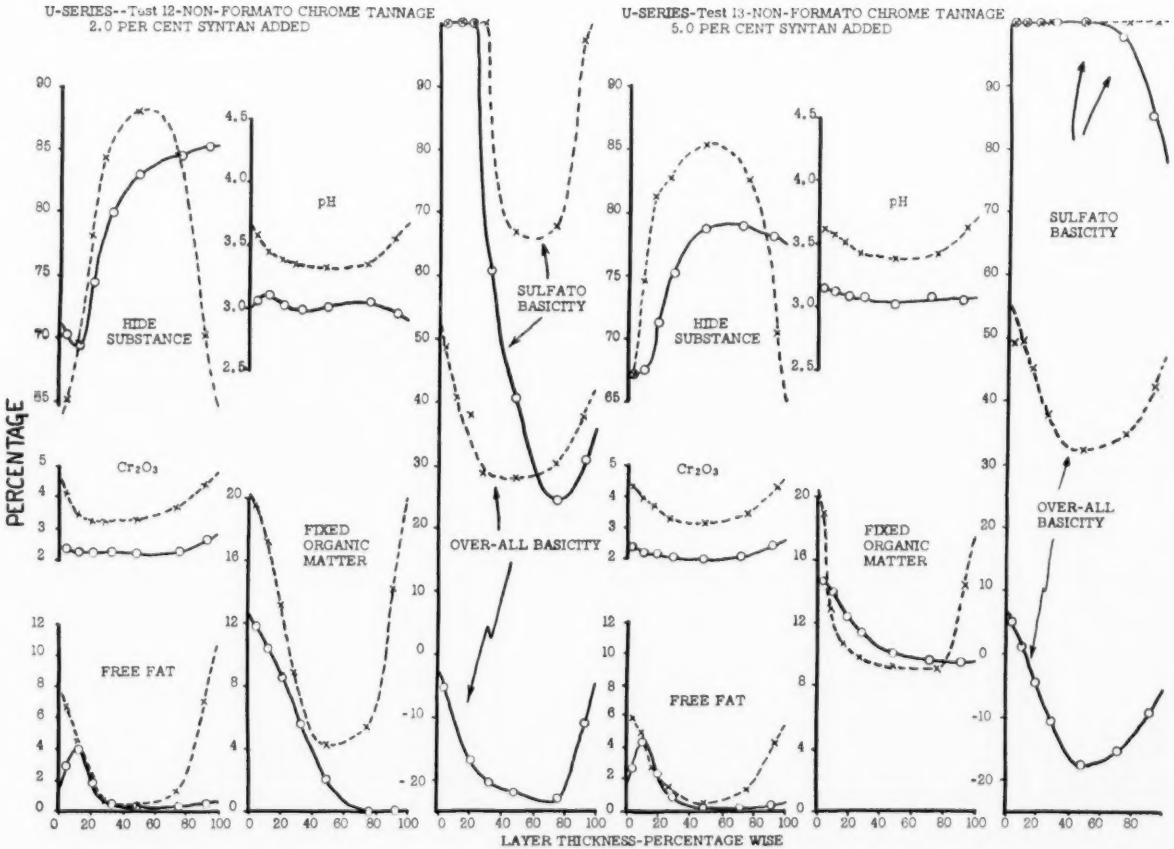

U-SERIES - NON-FORMATO-CHROME TANNAGE WITH ADDITIONS OF SYNTAN TO CHROME LIQUORS - AGED ONE WEEK
BLUE o—o CRUST x--x
U-SERIES--Test 10-NON-FORMATO CHROME TANNAGE
0.5 PER CENT SYNTAN ADDED
U-SERIES--Test 11-NON-FORMATO CHROME TANNAGE
1.0 PER CENT SYNTAN ADDED
SULFATO BASICITY
pH
HIDE SUBSTANCE
Cr_2O_3
OVER-ALL BASICITY
FIXED ORGANIC MATTER
FREE FAT
PERCENTAGE

FIGURE III


U-SERIES--Test 12-NON-FORMATO CHROME TANNAGE
2.0 PER CENT SYNTAN ADDED
U-SERIES-Test 13-NON-FORMATO CHROME TANNAGE
5.0 PER CENT SYNTAN ADDED
PERCENTAGE
HIDE SUBSTANCE
pH
SULFATO BASICITY
Cr_2O_3
FIXED ORGANIC MATTER
OVER-ALL BASICITY
FREE FAT
LAYER THICKNESS-PERCENTAGE WISE

sulfato basicity is markedly changed with increasing amounts of added neutral syntan as might be expected and the over-all change in this factor is greater than was the case when neutral syntan was merely added to the chrome liquor prior to tannage. This change should be expected, since upon heating the mixture, of syntan and chrome liquor, the syntan anions are literally driven into the chromium complex much more readily than would be the case of merely adding the syntan to the chrome liquor at normal temperatures. This particular fact can be readily seen by a study of Test 5, Figure I. The data relative to Test 5 further show that during the primary chrome tannage practically no sulfato groups were evident. However, due to the chrome retannage (after the syntan-formato chrome tannage) the retannage shows the presence of sulfato groups in the center layers of the skin.

The over-all basicity of the leather in the "blue" is not materially affected until some 5 per cent of the neutral syntan has been added. For the leather in the "crust" the over-all basicity increases very gradually with the increase in syntan. The real increase being in the grain and flesh layers—the center layers being affected but little in any case. The syntan additions affect the distribution of the natural fat. As can be seen from Figure I, the fat take-up during fat-liquoring is affected by the increasing syntan additions. This decrease is especially noticeable in the grain layer. Correlating the fat content with the "crust" sorting evaluation (Figure IV) it will readily be seen that the temper and fullness of the leather are low, even for the control (no syntan added) which may mean that the addition of more fat liquor or richer oil could alter these sorting evaluations. These same sorting evaluations obtain even for the finished leather though temper and fullness have improved to some extent.

Crackiness of leather increases with syntan addition but this factor might be better if more oil had been used in the fat-liquor.

The sorting evaluation index—Figure IV, as judged from the finished leather data would appear to indicate: (1) as far as break (tightness) and grain smoothness are concerned, all of the syntan additions gave passably good leather; whereas one per cent syntan addition seems to be the limit relative to fullness and temper are concerned.

Tests 6, 7, 8, and 9 of Series U constitute another partial series of formato-syntan-chrome tannages, in which the syntan was added to the chrome liquor in the cold and allowed to age one week before use. This small series of tests should be compared with that of Figure I and a careful study of the stratigraphic charts shown in Figure II will indicate some rather striking differences. Using Test 1 of Figure I as a control test, it will be seen that while the chromic oxide distribution, layerwise, is essentially a straight line in all of the stratigraphic charts, there is a real decrease in the amount of Cr_2O_3 fixed in the leather. In other words, Test 1 shows approximately 3.25 per cent Cr_2O_3 fixed, whereas Tests 6, 7, 8, and 9 indicate a gradual decrease in Cr_2O_3 to an approximate 2.6 per cent, indicative of what has been found

FIGURE IV - SORTING EVALUATION INDEX - SERIES U

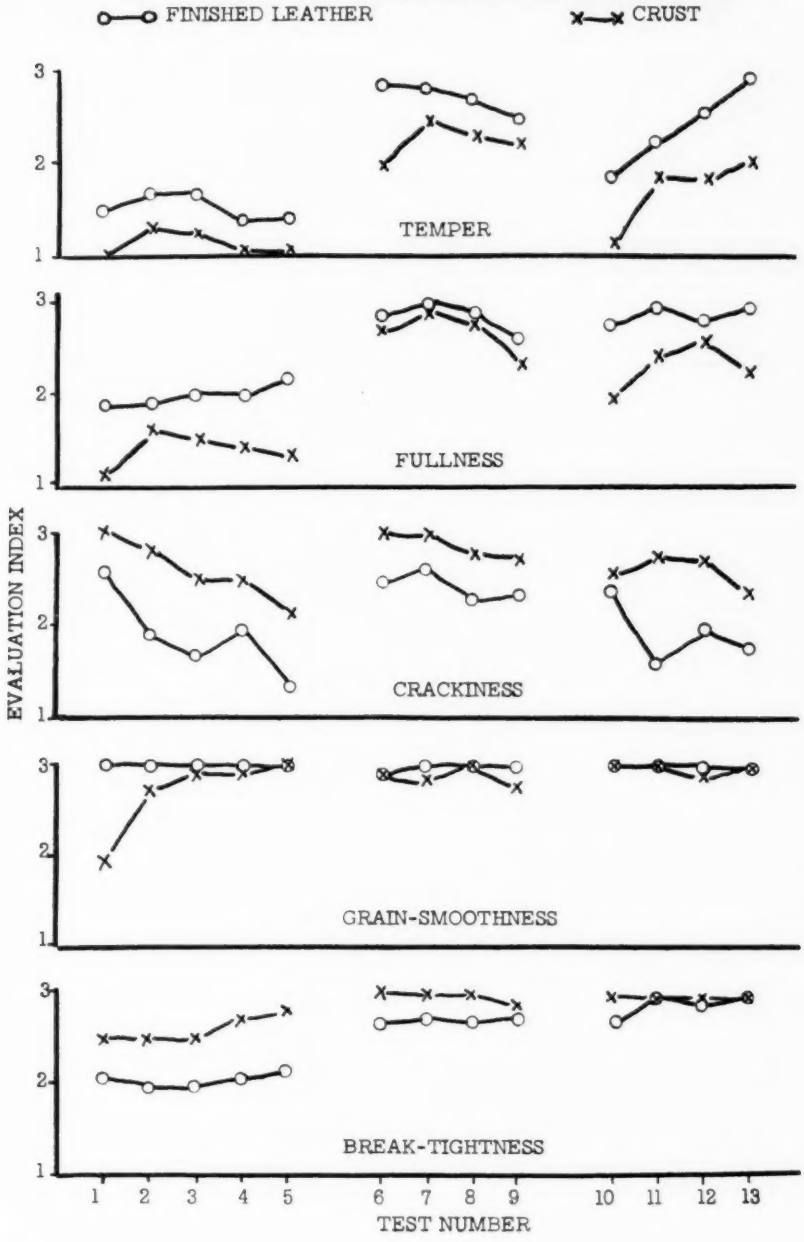
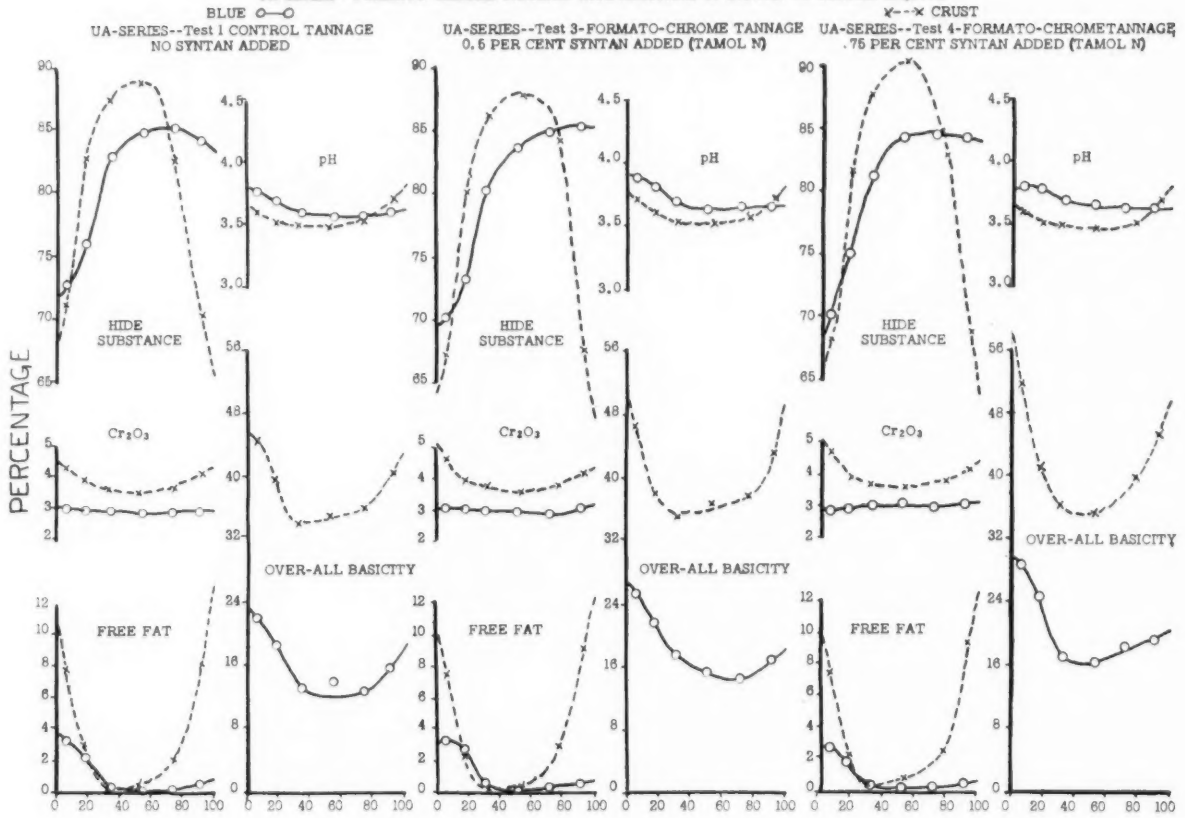
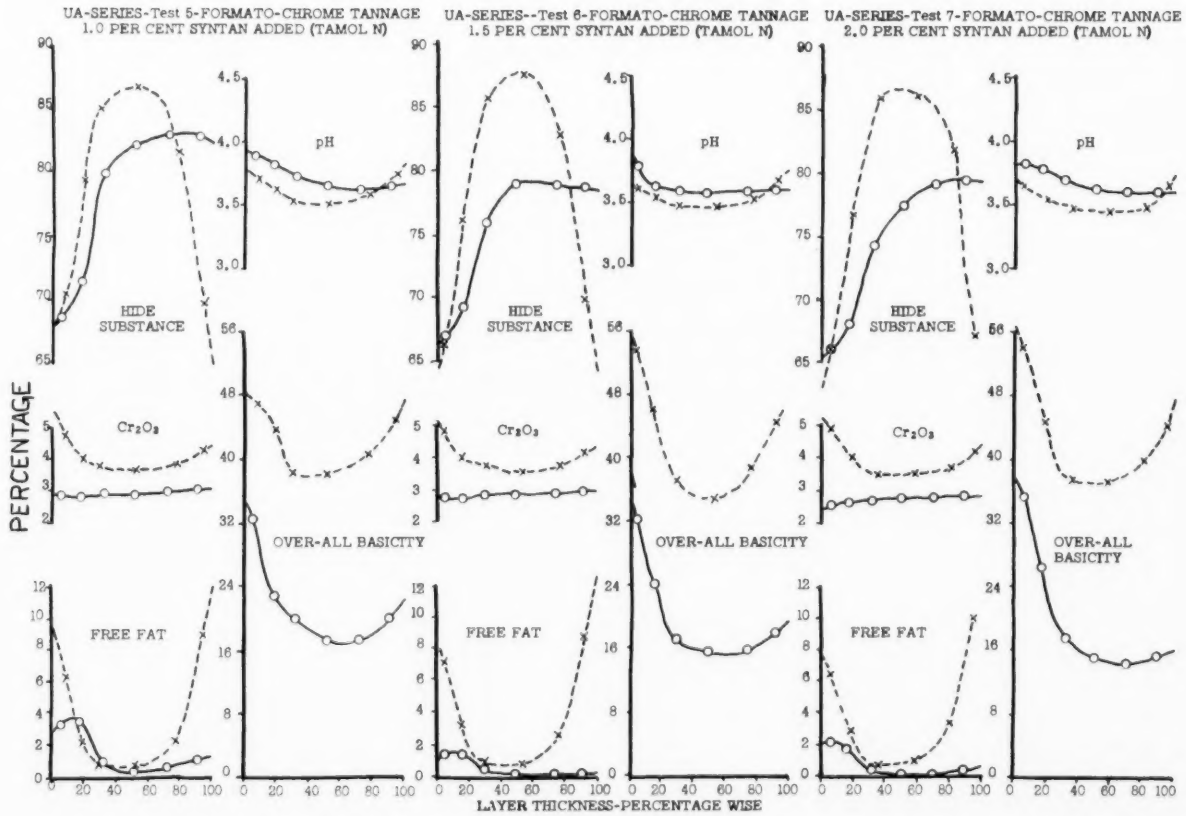


FIGURE V

UA-SERIES - FORMATO-CHROME TANNAGE WITH ADDITIONS OF SYNTAN TO CHROME LIQUORS




UA-SERIES-Test 5-FORMATO-CHROME TANNAGE
1.0 PER CENT SYNTAN ADDED (TAMOL N)
UA-SERIES--Test 6-FORMATO-CHROME TANNAGE
1.5 PER CENT SYNTAN ADDED (TAMOL N)
UA-SERIES-Test 7-FORMATO-CHROME TANNAGE
2.0 PER CENT SYNTAN ADDED (TAMOL N)
PERCENTAGE
HIDE SUBSTANCE
pH
Cr_2O_3
OVER-ALL BASICITY
FREE FAT
LAYER THICKNESS-PERCENTAGE WISE

for neutral syntan additions in previous investigations. In other words, allowing the chrome liquor to age in the presence of neutral syntan does not give the same results, during the tanning process, as the heat treated syntan-chrome liquor previously discussed.

The over-all basicities of the leathers in the "blue" are considerably altered especially in the center layers (these tests were taken after splitting and shaving). The over-all basicities of the leather in the "crust" state indicate a gradual increase in the grain and flesh (really the center layers of the original hide) layers.

The sorting evaluation indexes for Tests 6, 7, 8 and 9, as shown in Figure IV are decidedly better than those given for Tests 1, 2, 3, 4, and 5. This is especially true for crackiness, fullness, and temper. The sorting data appear to indicate that small additions of syntan are preferable to larger additions.

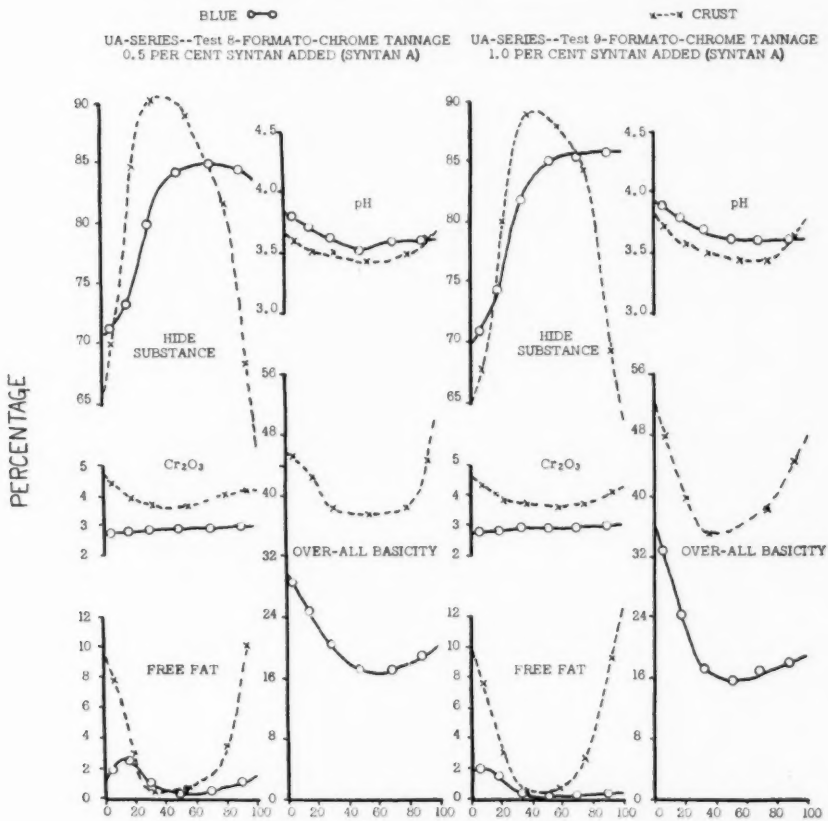
It might, therefore, be said that aging the chrome liquor in the presence of the neutral naphthalenic syntan has little or no advantage over the original way proposed in previous series, namely adding the syntan to the chrome liquor and its immediate use. With aging, however, the basic chromium sulfate complex deposited or fixed in the leather in the original tannage is changed to a basic syntan anion chromium complex since the sulfato groups decrease drastically with increasing amounts of added neutral syntan.

Tests 10, 11, 12 and 13 constitute a third partial series of series U and these tests are of the non-formato-syntan-chrome tannage type, as has been the case for all non-formato-chrome tannage tests, the syntan plays a very drastic role with regard to the chromic oxide fixation. However, by aging the chrome liquor in the presence of syntan for 1 week, the very erratic deposition of chrome oxide has been eliminated but the decreased fixation with increasing amounts of syntan still obtain as can be noted from the stratigraphs. The leather in the blue shows an over-all basicity far different from that of the formato-chrome tannage tests. Namely this factor has changed from positive over-all basicities to drastic negative ones, and therefore, the leather must have decidedly different over-all characteristics. In the crust conditions, the over-all basicity changes to a normal type, increasing to some extent with increasing amounts of syntan. It should be noticed that the sulfato basicities of the leather in the blue and the leather in the crust conditions are quite different from those values when formate had been used.

The sorting evaluation indices indicate increasing temper with increasing amounts of syntan, a very high value for fullness, a very erratic value for crackiness, an excellent value for grain-smoothness, and break. The data obtained for this partial series agree well with previous data taken for syntan additions to non-formato-chrome liquors.

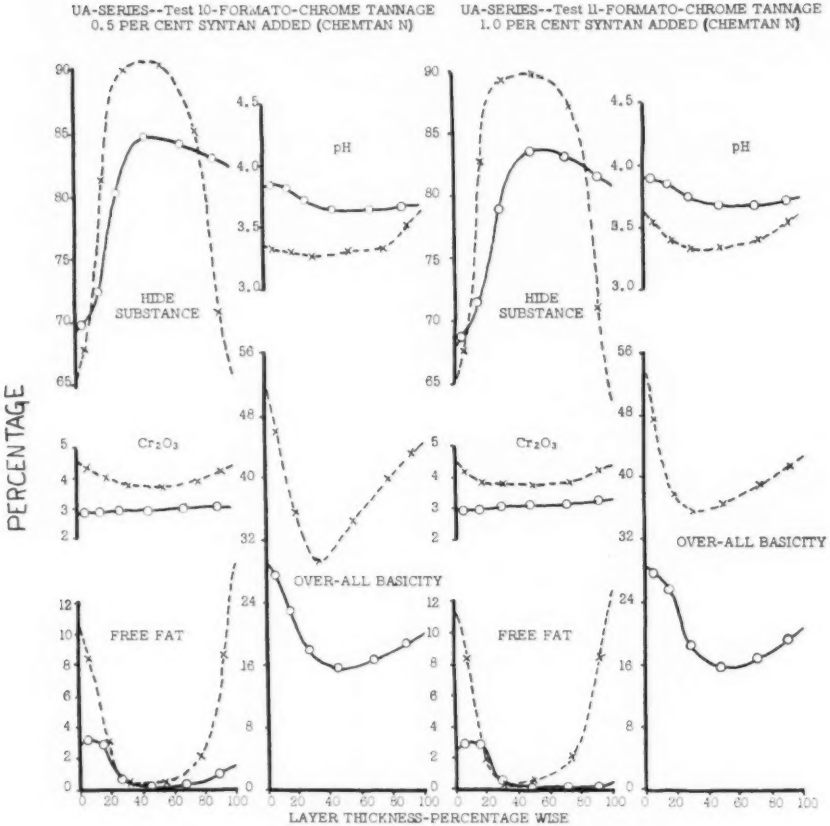
Since the sorting evaluation of the partial series, Tests 1, 2, 3, 4, and 5 appeared somewhat low especially as regards temper and fullness and further since these low values may be a raw stock condition, certain of these tests were repeated and will be discussed later under the UA-series.

FIGURE VI
UA-SERIES - FORMATO-CHROME TANNAGE WITH ADDITIONS OF DIFFERENT MANUFACTURED SYNTANS TO CHROME LIQUORS



The UA-series of some 11 tests were made so as to repeat certain tests of the U-series and to determine if various neutral naphthalenic syntans were interchangeable for tannery use. For these tests all were of the formato-chrome tanning type and no comparisons were made without formate being present. As in the U-series, some 200 pounds "white weight" stock was tanned as previously outlined and made into the same type of leather. The particulars of the 11 different tannages are given in Table IV. In all cases the particular syntan was dissolved in 3 quarts of water at 175° F and added to the chrome liquor before using.

FIGURE VI
UA-SERIES - FORMATO-CHROME TANNAGE WITH ADDITIONS OF DIFFERENT MANUFACTURED SYNTANS TO CHROME LIQUORS



The control data taken during the combined Bate-Pickle-Tan process are shown in Table V.

The partial UA-Series, Tests 1 - 7, shown in Figure V indicate that the Cr_2O_3 fixation layerwise (in the "blue" state) is a straight line function and is but little affected until the syntan additions have reached 1.5 per cent, above this figure the Cr_2O_3 decreases. The over-all basicity figure is increased in the grain layer as the amount of syntan is increased for the leather both in the "blue" and "crust" state. Again as shown for the U-Series the natural fat is redistributed. The fat taken up, during fat liquoring, is somewhat decreased with increase in syntan—compare Test 7 with Test 1.

TABLE IV

Showing Variations in the UA-Series

Test	No. Sides	Weight	Formate	Syntan	Neutralization
1	10	196	2%	None	36 oz. $NaHCO_3$
3	11	200	2%	0.5% Tamol N	35 oz. $NaHCO_3$
4	11	202	2%	0.75% " "	34 oz. "
5	11	202	2%	1.0% " "	33 oz. "
6	10	198	2%	1.5% " "	36 oz. "
7	10	200	2%	2.0% " "	34 oz. "
8	10	202	2%	0.5% Syntan A	36 oz. "
9	11	204	2%	1.0% " "	35 oz. "
10	11	210	2%	0.5% Chemtan N	36 oz. "
11	11	204	2%	1.0% " "	36 oz. "

Tamol N—Rohm and Haas
Syntan A—American Cyanamid
Chemtan N—Chemtan Company

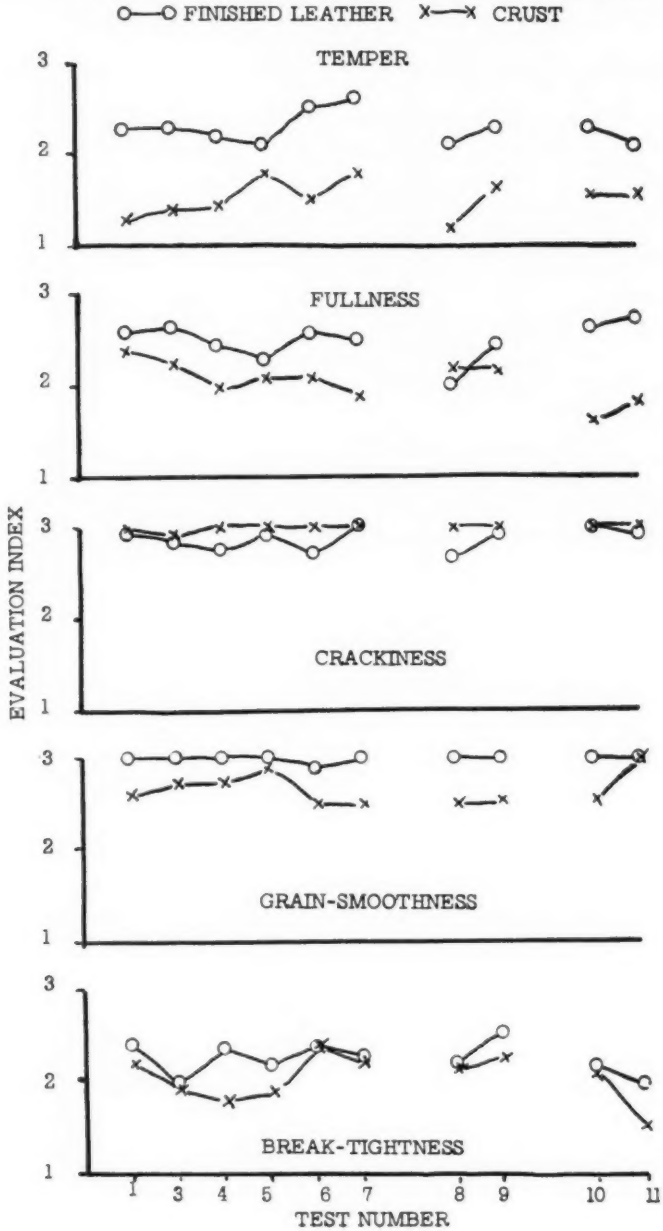
TABLE V

Test	After Bate	After Pickle	After Tan	After Neutralization	Shrink Temp °C
1	8.60	3.31	3.08	3.95	100.5
3	8.68	3.43	3.20	4.00	102.0
4	8.69	3.41	3.19	3.92	100.0
5	8.62	3.43	3.21	3.92	101.0
6	8.55	3.30	3.09	3.82	100.5
7	8.59	3.29	3.11	3.80	99.5
8	8.57	3.32	3.12	3.90	100.5
9	8.51	3.33	3.17	3.84	101.5
10	8.68	3.36	3.20	3.99	100.5
13	8.70	3.40	3.18	3.92	103.0

Test 8, 9, 10, and 11 of Figure VI, form another partial series and show the effect of several neutral naphthalenic syntans of different manufacturers. These data indicate that as far as adjuncts during chrome tanning, they can be used interchangeably as judged from the chemical data.

Figure VII shows the sorting evaluation indices for leather in the "crust" and in the "finished" state. A study of the sorting data for the leather in the "crust" state shows that in most cases the three different neutral syntans, give about the same general sorting index figures; for break or tightness Tests 8 and 9 are a little better than 3 and 5, and 10 and 11, for smoothness Test 5 and 11 are better than 8 or 9 (1 per cent additions of the three different syntans) ; for fullness, the one per cent addition gave more or less the same value (Tests 5, 9 and 11) with Test 9 giving slightly better index values;

FIGURE VII-SORTING EVALUATION INDEX - SERIES UA



and for temper, the one per cent addition of the three syntans gave essentially the same value. For the various test leathers in the "finished" state and considering only the one per cent additions; for break Test 9, for fullness Tests 10 and 11; and for temper Tests 9 and 10. However relative to the temper factor alone Tests 6 and 7 (greater than 1 per cent addition) gave better values.

2—Series S—The Effect of Vegetable Tanning and Synthetic Replacement Materials When Used as Adjuncts During Chrome Tanning

In all of the previous study relative to added adjuncts during chrome tanning, we have confined ourselves to the synthetic naphthalenic syntans because of their various uses suggested at one time or another in this field. In order to round out the picture, it was decided to investigate the effect of some general vegetable tanning extracts and so called synthetic replacement extracts as adjuncts in the chrome tanning process. For these studies, a wattle extract (Chembark LW) and Orotan TV were used. These materials were added to the regular sugar reduced chrome liquor just prior to its addition to the drum. Both non-formato and formato chrome tannages were employed. Table VI shows the particulars of some 13 different tests in this series.

TABLE VI

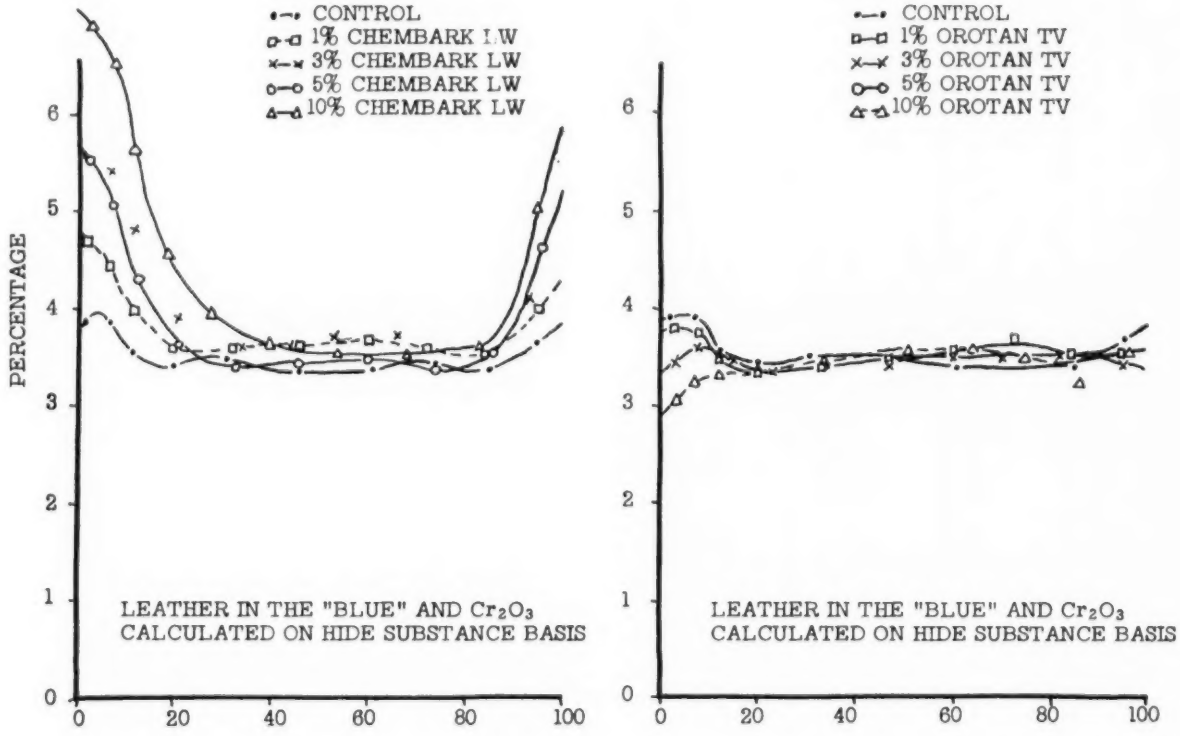
Test No. Control	Formate	Tanning Material	Neutralization
1	None	None	21 oz. $NaHCO_3$
2	None	1% Orotan TV	24 oz. "
3	None	3% Orotan TV	21 oz. "
4	None	5% Orotan TV	26 oz. "
5	2%	None	31 oz. "
6	2%	1% Orotan TV	30 oz. "
7	2%	3% Orotan TV	28 oz. "
8	2%	5% Orotan TV	32 oz. "
9	2%	10% Orotan TV	35 oz. "
10	2%	1% Chembark LW	32 oz. "
11	2%	3% Chembark LW	35 oz. "
12	2%	5% Chembark LW	33 oz. "
13	2%	10% Chembark LW	38 oz. "

Orotan TV—(Rohm and Haas)
Chembark LW—(Chemtan Company)

The control data taken during the combined Bate-Pickle-Tan process are given in Table VII.

FIGURE VIII

S-SERIES - EFFECT OF VEGETABLE AND/OR VEGETABLE REPLACEMENT MATERIALS USED AS ADJUNCTS IN CHROME TANNING ON Cr_2O_3 DISTRIBUTION



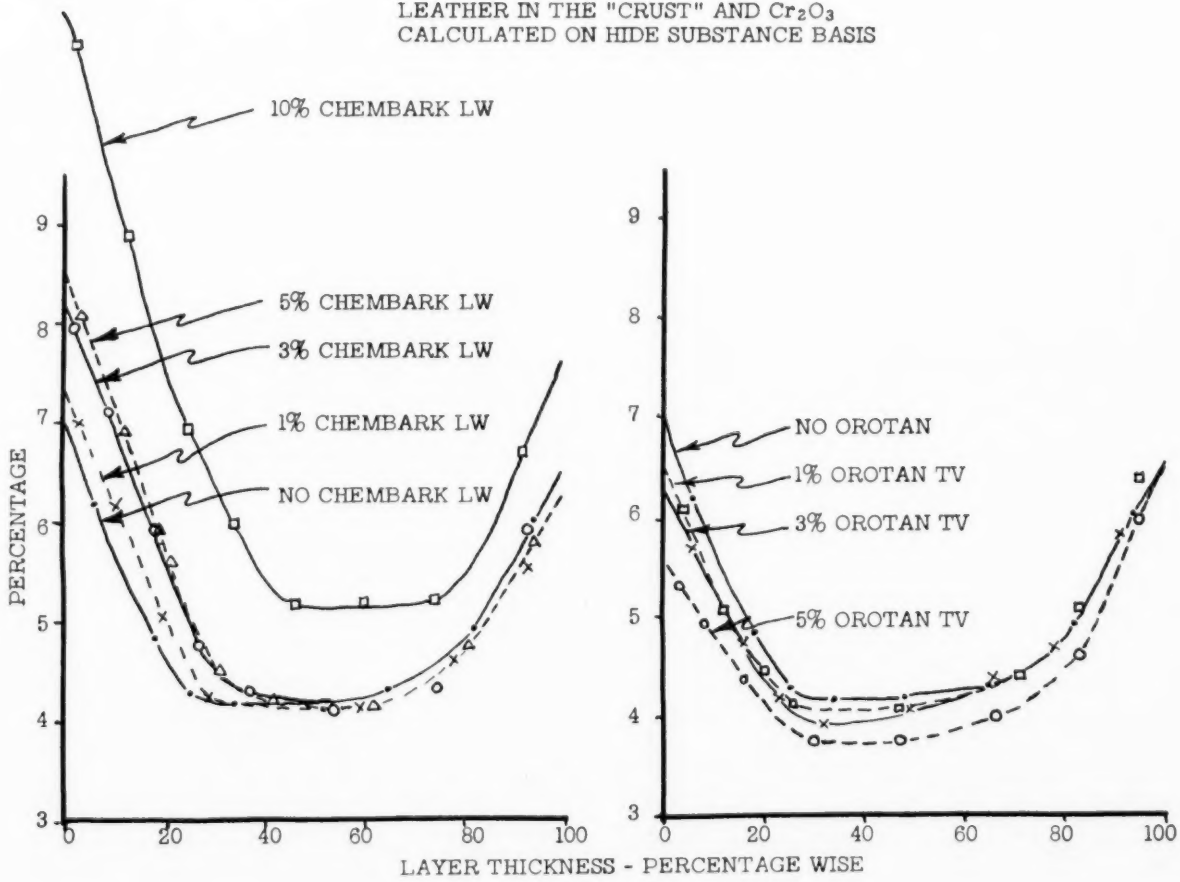

LEATHER IN THE "CRUST" AND Cr_2O_3
CALCULATED ON HIDE SUBSTANCE BASIS
10% CHEMBARK LW
5% CHEMBARK LW
3% CHEMBARK LW
1% CHEMBARK LW
NO CHEMBARK LW
NO OROTAN
1% OROTAN TV
3% OROTAN TV
5% OROTAN TV
PERCENTAGE
LAYER THICKNESS - PERCENTAGE WISE
3
4
5
6
7
8
9
0
20
40
60
80
100

TABLE VII

Test No.	After Bate	After Pickle	After Tan	After Neutralization	Shrink Temp. °C
1	8.70	1.52	2.30	3.00	82.0
2	8.58	1.42	2.17	3.00	78.0
3	8.50	1.60	2.36	3.10	76.0
4	8.60	1.40	2.08	2.87	84.0
5	8.68	3.38	3.23	4.00	101.5
6	8.72	3.36	3.28	4.00	100.5
7	8.72	3.50	3.31	3.94	101.0
8	8.70	3.38	3.18	3.91	100.0
9	8.52	3.40	3.11	3.80	95.0
10	8.60	3.40	3.19	3.94	100.5
11	8.58	3.37	3.13	3.88	101.5
12	8.66	3.42	3.24	3.78	102.0
13	9.00	3.58	3.23	3.70	99.0

Figures VIII and IX summarize the chemical data taken for this series of tests. Figure VIII shows the effect of the vegetable extract and the synthetic replacement material on the Cr_2O_3 fixation—both for the leather in the "blue" and the "crust" state. These data indicate strikingly that Cr_2O_3 fixation in the grain and flesh layers is greatly increased if vegetable extract is present during the chrome tannage while the reverse is true if the replacement (Orotan TV) material is present.

Figure VIII shows the layer-wise distribution of Cr_2O_3, based on hide substance values, for the various tests made in this series for both the leather in the "blue" and in the "crust" state. The significant facts are: (1) the addition of vegetable tanning extracts to the chrome liquor causes a greater fixation of the chromium salt with the skin fibers—in other words there is an association of the certain vegetable tannin molecules with the basic chromium salt which results in greater fixation in the grain and flesh layers of the skin; (2) as the vegetable extract is increased, the fixation, noted in (1) becomes greater; (3) additions of vegetable extract up through 5.0 per cent do not influence the fixation in the center layers of the skin but 10 per cent addition effects or increases even the center layers; and (4) the use of replacement materials such as Orotan TV decreases the fixation of the chromium salt in the grain layer and this decrease in fixation becomes more and more apparent as the additions of Orotan increase.

Figure IX shows the effect of Orotan additions to both the non-formato and formato-chrome tannage, wherein it can be seen that the effect is identical. This particular phase of the study will be discussed in some detail later in regard to the SA-series of tests.

Figure X gives the sorting evaluation data relative to this series of tests for both the leather in the "crust" and "finished" condition. Tests 1, 2, 3,

FIGURE IX

EFFECT OF VEGETABLE TANNING REPLACEMENT MATERIAL ADDED TO CHROME LIQUORS ON Cr_2O_3 FIXATION

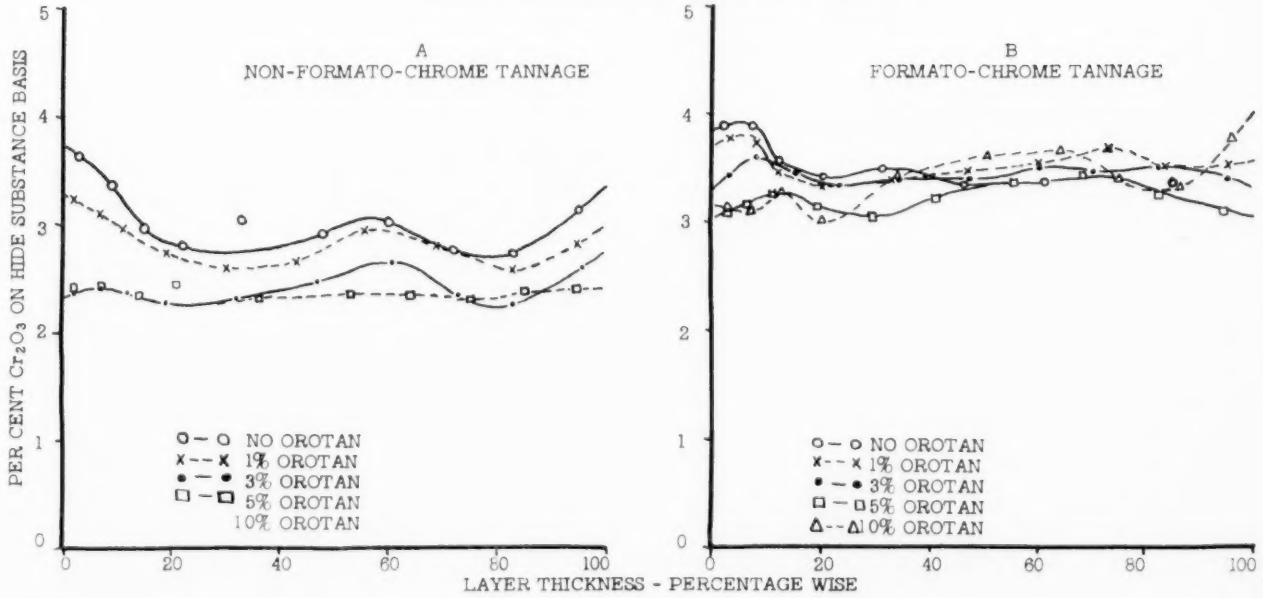
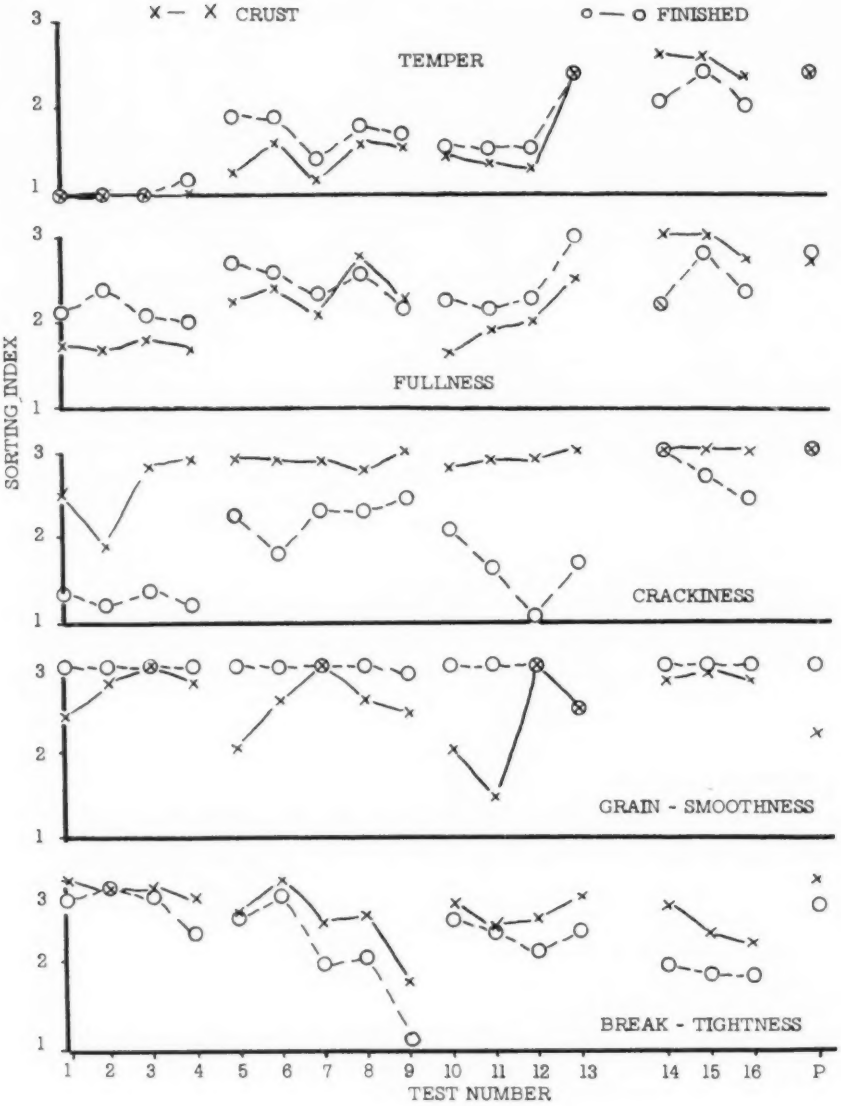


FIGURE X
SERIES S - SORTING EVALUATION INDEX



and 4 represent the orotan additions in the non-formato-chrome tannage and show good "break" and smoothness, but poor "fullness and temper". Tests 5 through 9 show the evaluation data for Orotan additions to the formato-chrome liquors. In general the leather is better but the small differences may be due to a raw stock problem. Tests 10 through 13 are for vegetable extract additions and in these cases Tests 12 and 13 appear the best. Tests 14, 15 and 16 are for formato chrome tannage using Tanolin R (prepared commercial chrome liquor) as the source of the basic chrome liquor. This test marked "P" is for regular production leather of the same type and character. The sorting evaluation for this entire series appeared to vary and there were erratic differences not in line with experience and the authors believe the raw stock variable was the real cause of the variations seen in Figure X.

The chemical data as shown by Series S was of such nature as to be of interest and of intriguing nature and therefore the series was repeated with certain modifications and these changes are given in the SA-Series as shown by Table VIII.

TABLE VIII

Particulars of the SA-Series

Test No.	No. Sides	Weight	Formate	Tanning Material	$NaHCO_3$	pH
1	9	196	2%		31 oz.	4.0
2	9	204	2%	3% Orotan TV	28 oz.	4.0
3	9	200	2%	5% Orotan TV	32 oz.	4.0
4	9	200	2%	5% Leather Product X59A	32 oz.	4.0
5	13	200	2%	6.38% Chemtan W-2	38 oz.	4.0
6	10	202	2%	10% Orotan TV	37 oz.	4.0
7	10	198	2%	3% Chembark LW	36 oz.	4.0
8	10	208	2%	5% Chembark LW	36 oz.	4.0
9	9	200	2%	5% Twecotan XX	42 oz.	4.0
10	13	198	2%	5% Liq. Maratan B	32 oz.	4.0
11	13	200	2%	10% Chembark LW	38 oz.	4.0

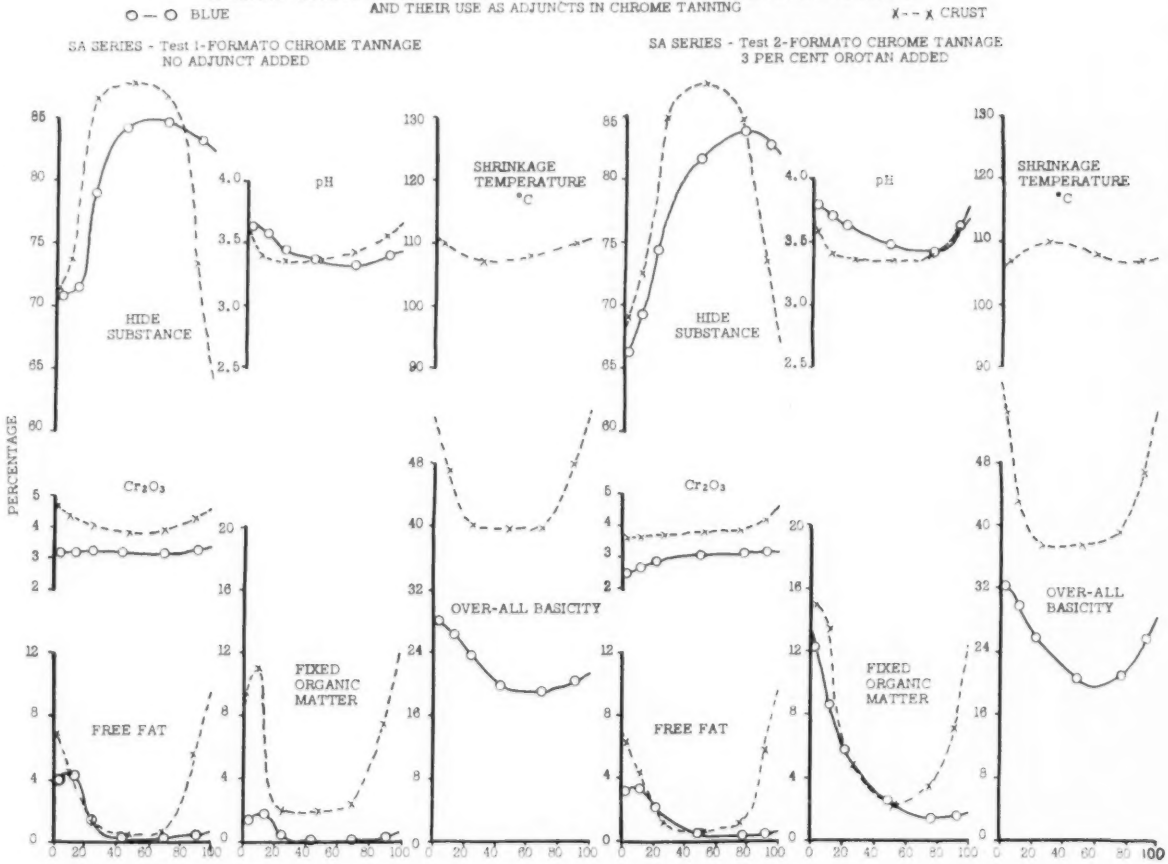
Orotan TV—Rohm and Haas
Maratan B—Marathon Corporation
Leather Products X59A—American Cyanamid
Twecotan XX—American Cyanamid
Chemtan W-2—Chemtan Company
Chembark LW—Chemtan Company

The control data for the SA-Series is given in Table IX.

The stratigraphic data taken for the 11 tests of Series SA are shown in Figures XI, XII, XIII. A careful study of these stratigraphic data indicate certain trends: (1) the Orotan additions decrease the Cr_2O_3 fixation as previously shown in the S-Series of tests; (2) the Orotan additions appear to de-

FIGURE XI

SA SERIES - EFFECT OF CERTAIN SYNTHETIC VEGETABLE EXTRACT REPLACEMENT MATERIALS AND THEIR USE AS ADJUNCTS IN CHROME TANNING



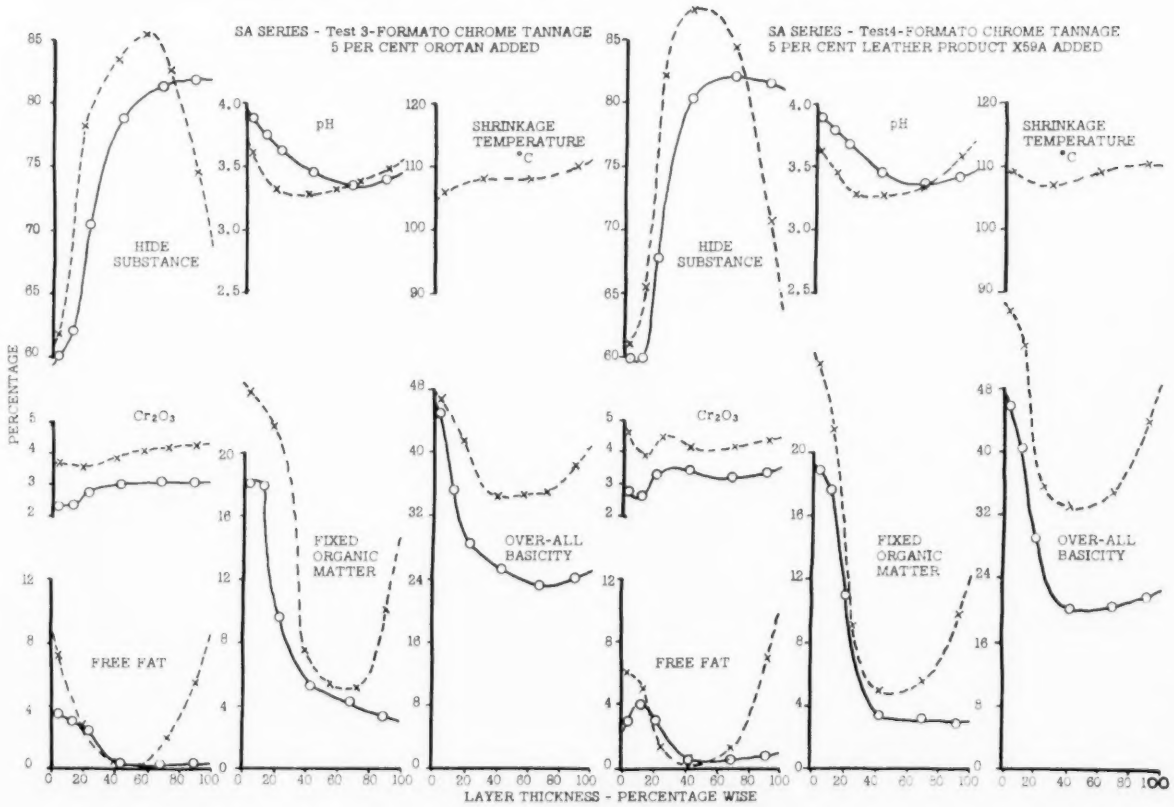
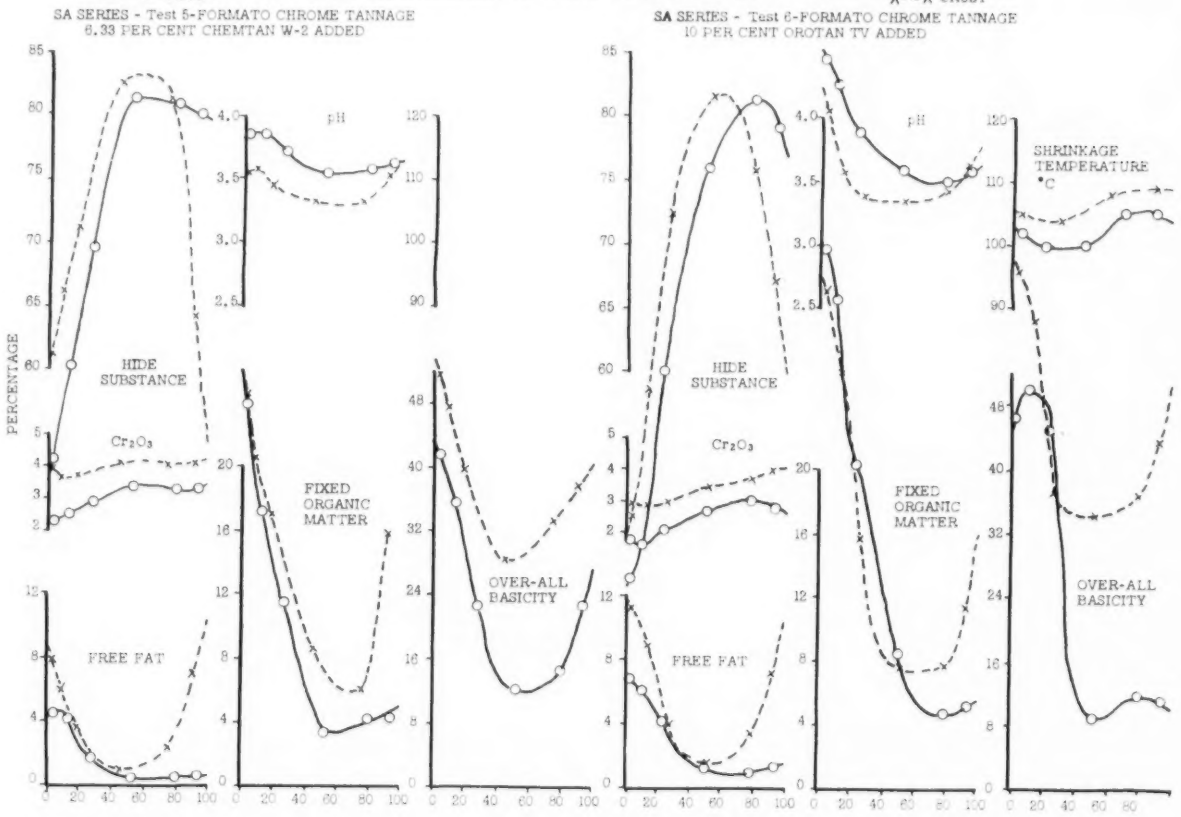

SA SERIES - Test 3-FORMATO CHROME TANNAGE
5 PER CENT OROTAN ADDED
SA SERIES - Test4-FORMATO CHROME TANNAGE
5 PER CENT LEATHER PRODUCT X59A ADDED
HIDE SUBSTANCE
pH
SHRINKAGE TEMPERATURE °C
Cr_2O_3
FIXED ORGANIC MATTER
OVER-ALL BASICITY
FREE FAT
PERCENTAGE
LAYER THICKNESS - PERCENTAGE WISE

FIGURE XII

SA SERIES - EFFECT OF CERTAIN VEGETABLE EXTRACTS AND SYNTHETIC VEGETABLE EXTRACT REPLACEMENT MATERIALS AND THEIR USE AS ADJUNCTS IN CHROME TANNING

O—O BLUE X-·-X CRUST



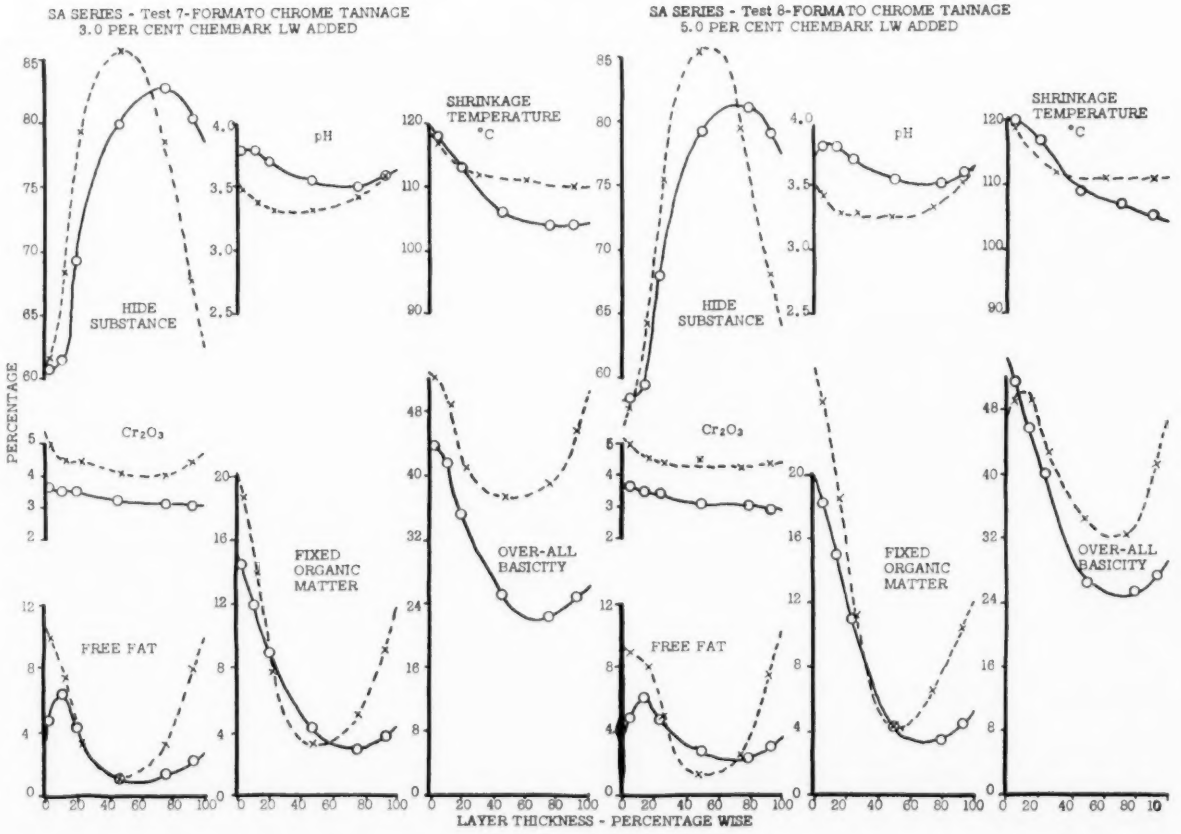

SA SERIES - Test 7-FORMATO CHROME TANNAGE
3.0 PER CENT CHEMBARK LW ADDED
SA SERIES - Test 8-FORMATO CHROME TANNAGE
5.0 PER CENT CHEMBARK LW ADDED
HIDE SUBSTANCE
pH
SHRINKAGE TEMPERATURE °C
Cr_2O_3
FIXED ORGANIC MATTER
OVER-ALL BASICITY
FREE FAT
PERCENTAGE
LAYER THICKNESS - PERCENTAGE WISE

FIGURE XIII

5A SERIES - EFFECT OF CERTAIN VEGETABLE EXTRACTS AND SYNTHETIC VEGETABLE EXTRACT REPLACEMENT MATERIALS AND THEIR USE AS ADJUNCTS IN CHROME TANNING

BLUE

CRUST

5A SERIES - Test 9-FORMATO CHROME TANNAGE
5.0 PER CENT TWEOTAN XX ADDED

5A SERIES - Test 10-FORMATO CHROME TANNAGE
5.0 PER CENT MARATAN R ADDED

5A SERIES - Test 11-FORMATO CHROME TANNAGE
10 PER CENT CHEMBARK LW ADDED

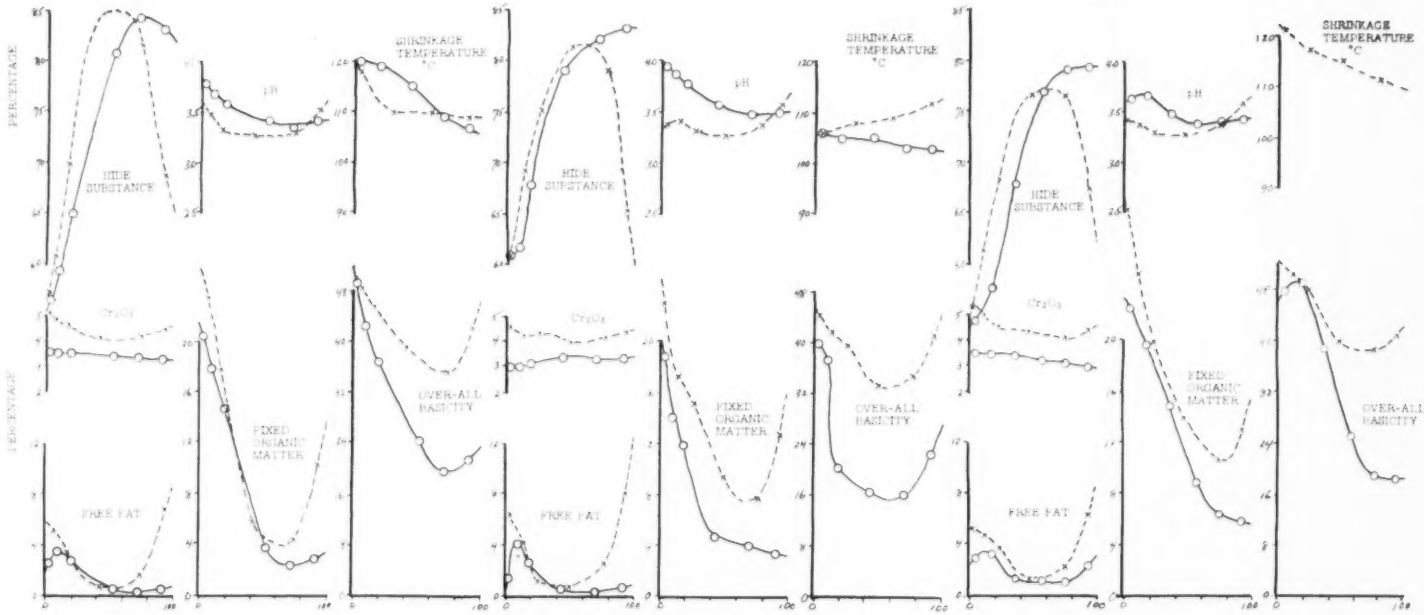


TABLE IX

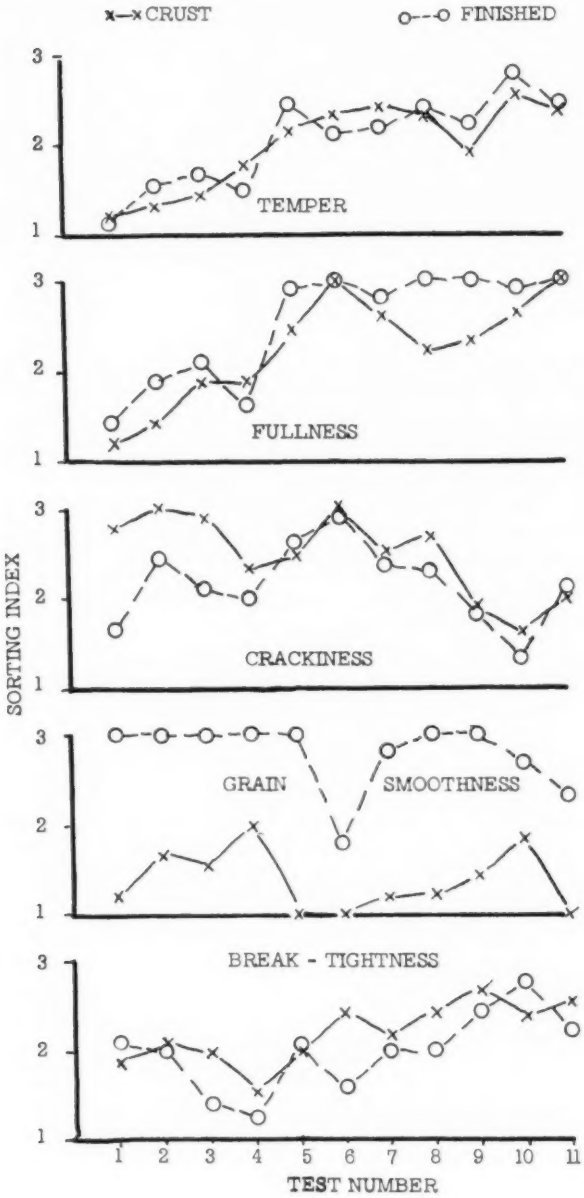
Test No.	After Bate	After Pickle	After Tan	After Neutralization	Shrink Temp °C
1	8.43	3.40	3.17	4.01	103.5
2	8.38	3.43	3.20	3.91	101.0
3	8.50	3.42	3.17	3.92	99.0
4	8.40	3.47	3.22	4.03	102.0
5	8.62	3.52	3.17	4.01	100.5
6	8.42	3.32	3.08	3.90	95.0
7	8.51	3.40	3.26	4.10	101.0
8	8.57	3.32	3.18	3.97	102.5
9	8.46	3.32	3.15	3.89	101.0
10	8.58	3.47	3.30	4.08	104.0
11	8.60	3.49	3.26	4.01	104.5

crease the shrinkage temperature of the finished leather; (3) similar products (X59A and Chemtan W-2) give like results to those of Orotan; and (4) all of these products influence the fixed organic matter as might be expected. Products related to the vegetable tanning extracts increase the Cr_2O_3 fixed in about the same amount as previously shown in Series S. The over-all basicity is in general increased by both the natural and synthetic vegetable type tanning materials. This is an expected result since both types of material affect the sulfato groups of the chrome liquors.

Figure XIV gives the sorting evaluation data for the eleven tests of the SA-Series. A break down of these data indicate: (1) in the main the "tightness" of the leather in Tests 3, 4, 6, 7, 8, 9, and 11 decreased between the "crust" and the finished leather whereas Tests 1, 2, 5, and 10, this condition was in the reverse order; (2) regarding smoothness Tests 1, 2, 3, 4, 5, 7, 8 and 9 had almost a perfect value—that is a value of 3.0; (3) with regard to fullness and temper, Tests 5 through 11 showed real promise. For the over-all picture, Tests 5 and 6 gave the best picture for the synthetic replacement materials and Test 10 for the vegetable tanning material. It should be pointed out that all of the natural vegetable extracts used gave real promise. The "cracky" condition obtaining could undoubtedly be corrected by certain changes in process.

In both the S and SA Series, it was shown that the natural and synthetic type of vegetable tanning material affect the fixation of the basic chromium salt on the hide fiber. Remembering that the adjunct material was added directly to the 40 per cent sugar reduced chrome liquor, it is natural to assume that these added materials drastically changed the nature of the chromium complexes in that liquor. It has long been postulated that there are *tanning* and *non-tanning* complexes in any commercial chrome liquor and it is reasonable to assume that the addition of either the natural or synthetic variety

FIGURE XIV
SERIES SA - SORTING EVALUATION INDEX



of so called vegetable tanning materials will change the ratio of the different complexes. Whether this change is caused by the interchange of one ligand for another in the chrome liquor or the natural or synthetic material is hydrogen bonded with the chromium complex may be a question of pure speculation. It is known however that the chrome liquor which contains natural vegetable tanning material causes a higher Cr_2O_3 fixation than the regular chrome liquor and in turn this same liquor containing the synthetic material causes a lessened Cr_2O_3 fixation. It would appear that the natural vegetable tanning materials act, (as far as Cr_2O_3 fixation obtains) in a similar manner to phthalates but it is doubtful if any stable ring occurs in its association with the chromium salt. In all probability the higher Cr_2O_3 fixation imparted is due to non ring forming polydendate ligands[2]. It should be pointed out that these non ring forming ligands may be associated to some extent due to actual replacement of sulfate anions and perhaps to some extent due to hydrogen bonding with the basic chromium complex.

On the other hand the addition of the synthetic replacement material, due to their previous chemical treatment, during synthesis form certain *very stable* ring structures with the polydendate materials such that there can be no replacement of the associated ligands by the carboxyl groups of the protein side chains and for this reason less fixation of chromium salt obtains. Such a postulation could be in good agreement with recent ideas of Shuttleworth[2].

Summary

The cooperative investigations relative to the effects of various *neutral naphthalenic syntans* as adjuncts in chrome tanning were continued and the data obtained are reported herein.

These data show rather conclusively that conservative use of the different neutral syntans have a beneficial effect on chrome tanning—especially if the tannage be of the formato-chrome tanning type. The use of the syntan lends itself especially in the combined "bate-pickle-and tan" process.

The use of natural vegetable tanning materials and synthetic replacement materials were investigated in the same manner as were the neutral naphthalenic syntan studies. It was found that the natural tannins when used as adjuncts during chrome tanning gave an increased Cr_2O_3 fixation in the grain and flesh layers. Comparison with phthalate-chrome complexes was made but it was stressed that the tanning chrome complexes formed were probably not of the same type as those resulting from phthalate additions. The use of synthetic replacement material additions caused a decrease in Cr_2O_3 fixation in the grain and flesh layers. It was pointed out that the synthetic material in all probability formed extremely stable complexes—such that the associated ligands could not be replaced by the carboxyl groups of the protein side chains and thus some decrease in Cr_2O_3 fixation obtained.

In the interpreatation of these investigations, we have not touched upon the possible primary fixation of the vegetable tannins with the protein and have dealt only with the possible tannin-chrome complexes. It is quite possible that hydrogen bonding of part of the vegetable tanning materials with the protein occurs simultaneously with the coulombic combination of the tannin-chrome complexes. This fact will be dealt with in subsequent papers.

ACKNOWLEDGMENT

The writers take pleasure in thanking the American Cyanamid Company, the Diamond Alkali Company, the Mutual Chemical Company of America, and the Albert Trostel and Sons Company, for their wholehearted cooperation in these investigations. Without the inspiration, financial help, and cooperation between plant and laboratory, such studies could not have been presented.

BIBLIOGRAPHY

1. Theis, E. R., and Lotz, W. R., J. Amer. Leather Chem. Assoc. **47,** 219, (1952).
2. Shuttleworth, S. G. ibid., **47,** 387, (1952), ibid., **47,** 603, (1952), J. Soc. Leather Trades Chem. **34,** 410, (1950)., ibid., **36,** 292, (1952).

Received February 3, 1953

The Problem of Tannery Waste Disposal

HARRY H. REDLICH

Due to the ever growing interest in the problem of industrial waste disposal in Canada, the writer of this report was asked to prepare a brief summary of one aspect of the work, which has been done in the United States and in this country, to combat the serious situation arising from an exceptionally rapid industrial growth during the last decade. In the following report the author presents some of the problems of waste disposal which are related to the leather industry.

SUMMARY

1. The individual nature of any problem in tannery waste disposal precludes more than a brief outline of measures adaptable in the treatment of these wastes. A careful study of all phases of the problem is essential to the design of treatment works which will produce an effluent which can be assimilated readily by the stream into which the wastes are discharged. However a few general principles can be enumerated which are generally applicable to most tanneries.

(a) The volume of water used in the various tanning operations should be kept to a minimum. An attempt should be made to re-use some of the spent waters in the tannery, viz., the bate washes can in many instances be quite readily used as a make-up for the water employed in the lime vats.

(b) The liquid wastes should be discharged from the tannery 24 hours a day and if possible, on every day of the week, even if the tannery only operates on a 40-hour week.

(c) Often a vegetable tannery discharges its waste into a stream subject to marked seasonal variations in flow rates. In such a case the spent tan liquors should be separated from the remaining effluents and these highly putrescent tan liquors stored in open lagoons which are in turn discharged to the local stream only during periods of high water level. However, in some locations special permission must be obtained from the authorities for the prolonged storage of waste.

2. A tannery may be located in a small town which has a disposal plant only large enough to handle the domestic waste of the town population. In such instances, it may be advisable for the management of the tannery to come to a mutually satisfactory agreement with the local authorities to enlarge the sewage plant in existence, for the treatment of the tannery effluents.

3. It is now definitely established that adequate treatment of tannery sewage can be had, if the problems relating to each case are thoroughly studied. However, the cost of adequate treatment is great and the prospects of reducing the costs by reclaiming by-products or by changes in the tanning processes are not too encouraging. The tanning industry is faced with the fact that a concerted and widespread effort is now in progress to abate the pollution in our public watercourses and that tannery waste treatment is a necessary part of the general program.

4. The interested parties in Ontario may wish to investigate the advisability of establishing a tannery waste committee, composed of representatives of the tanning industry, the public health authorities and a number of experts, similar to that set up in most U. S. states.

Selecting the State of Pennsylvania as a representative example, the aim of such a committee may be to determine:

(a) The nature and polluting strength of the ingredients of tannery waste.

(b) The assimilating capacity of streams for this waste, untreated and treated in various degrees.

(c) Reasonable and practicable processes of treatment depending on the nature and location of the watercourses into which the wastes are discharged.

(d) Cost of data of construction and operation.

Such a committee would foster close co-operation between the tanners and

the authorities in the solution of the problem of waste disposal. It is emphasized that such a committee could utilize the impressive amount of work which has been done on this problem in the United States.

Introduction

Wastes have been carried away or disposed of by surface waters from earliest days. In recent years, due to the rapid growth of industrial and residential districts, many streams have become open sewers because of waste discharges from which adequate treatment has not been provided. Streams that once easily handled wastes from small industrial establishments are now unable to cope with the augmented volumes and diverse types of waste being produced. Practically all sections of the population make use of our water-courses in some way or other and therefore are highly interested that not too much refuse is discharged into them. It is generally believed that in our expanding social and industrial structure all those utilizing our surface waters should adopt a reasonable and constructive attitude towards this aim. No doubt water is a valuable commodity, but in many parts of the country its supply is definitely not unlimited and inexhaustible. Despite this only in exceptional cases economical use is made of our natural water supplies. The combined effects of deforestation and the increasing withdrawal of water for industrial and agricultural purposes have been lowering the water table at a dangerous rate in many sections of the country. To contribute willfully to the deterioration of the surface waters, by pollution which can be corrected, obviously is a shortsighted policy.

Composition and Properties of Tannery Wastes

Tannery wastes in particular are very strong wastes as compared to domestic sewage, as they contain constituents which complicate the method of disposal.

According to the "Industrial Waste Guide" of the Ohio River Pollution Survey, 100 lbs. of green salted hides, as received at a tannery will produce about 68 lbs. of finished leather. The remaining 32 lbs., more or less, is waste consisting of hair, trimmings, fleshings and shavings, all of which must be disposed of together with about 10 lbs. of lime and smaller amounts of other chemicals. Fortunately, most of the hair, trimmings, fleshings and shavings are reclaimed by the tanneries and can be sold for use in the manufacture of glue, grease, rug felt or binders. A substantial portion of these organic materials, however, reaches the liquid wastes and is responsible together with spent lime, sodium sulfide, soda ash, sulfuric acid and spent tan liquors for the obnoxious and detrimental character of the liquid wastes. It will be

noted that the effluents from the tanneries using the vegetable tan process have different characteristics from those using chrome chemicals in their process. Therefore the wastes from the two types of processes are dealt with separately in the subsequent discussion.

(*a*) *Effluent from Tannery Using the Vegetable Tan Process.*

It has been found that in the United States an average tannery of this type will discharge from 6 - 8 U. S. gallons of waste for each pound of raw hide processed. In terms of the biochemical oxygen demand tests, an important measure of potency, the waste discharge per pound of raw hide processed is equivalent to the sewage produced by a polualtion of .5 persons per day. A representative analysis of the total wastes will approximate the following:

Total Solids	7,000 parts per million
Volatile Solids (Portion of total solids which will volatilize upon ignition)	3,500 " " "
Suspended Solids (Portion of total solids suspended)	2,500 " " "
Settleable Solids (Volume of solids settling out in a given period of time)	8 volume per cent
Biochemical Oxygen Demand (Measure of organic pollution load)	1,200 parts per million
Color (American Public Health Association)	3,500 " " "
pH	13

If the above figures are compared with those of ordinary municipal sewage it will be seen that the strength of the tannery wastes is about 8 - 10 times as great. The strong alkalinity is due to the relatively large quantities of lime used in the beam house. The high Biochemical Oxygen Demand, usually referred to as B. O. D., has a tendency to deoxygenate the receiving stream and as a result aquatic life may be inhibited. Due to the usually strong discolouration caused by the spent tannins and the heavy suspended solids of the wastes, discoloured sludge banks may be formed in the receiving stream which may present an unsightly appearance. If iron is present in the receiving waters, dark green or inky blue precipitates may be formed due to the reaction of the tannins with the iron present in the water.

In recent years, however, synthetic tanning compounds, or so-called syntans, have shown promise of replacing some of the vegetable tanning materials most of which have to be imported. It is possible that this development, and other recent strides in research being conducted by the heavy leather industry (vegetable tan process) will result in some alleviation of the problem of discolouration by spent vegetable tan liquors.

(*b*) *Effluent from Tannery Using the Chrome Process*

Certain substances are contained in the effluents of both types of tanneries, but the effluents from the chrome tanning process are less harmful and offensive. Wastes from chrome tanneries have a B. O. D. value about 50% lower than the wastes from vegetable tanneries. The lower B. O. D. can be explained by the absence of the spent tan liquors which also accounts for the fact that wastes from chrome tanneries are usually not as highly coloured. If the tannery is operating smoothly, usually a not too high concentration of chrome will be found in the liquid wastes. Should the wastes be discharged directly into a watercourse, it may happen that when substantial concentrations of chrome do reach the rivers, these may exert a harmful effect on aquatic life. Such concentrations of chrome may also be toxic to the bacteria employed in the process of waste digestion, if the tannery effluents are treated in a sewage plant by biochemical means. Under normal conditions, any quantities of chrome which are discharged are readily precipitated as colourless hydroxides of chromium when the wastes containing the chrome are mixed with the highly alkaline beam house effluents

General Principles and Methods of Disposal of Tannery Wastes

It is very difficult to specify a general method of treatment which can be adopted by all tanneries. The design of a treatment works for a particular tannery will be influenced by a number of factors such as the type of process used in the tannery, its location, volume of wastes, availability of land, size and type of receiving stream, and the degree of treatment required by existing regulations. A careful appraisal of these factors is essential in the selection of treatment methods and units which can be expected to be effective and which would involve the lowest possible capital and operating costs.

In the tanning process itself a number of steps can be taken to ease the problem of waste disposal. Particular attention should be given to the possibility of reduction of volume of water used in the plant through elimination of indiscriminate use and the possible re-use of the relatively clean flow from the green stock pools and hair washer. Furthermore, good housekeeping is one of the prerequisites and a serious attempt should be made to separate out and reclaim, if possible, all solid matter in the waste, such as fleshings, trimmings, shavings and hair from the affluents of the beam house before they reach the drain.

Methods of Disposal of Liquid Wastes from a Typical Heavy Leather Tannery (Vegetable Tan Process)

(*a*) *Discharge into a Stream*

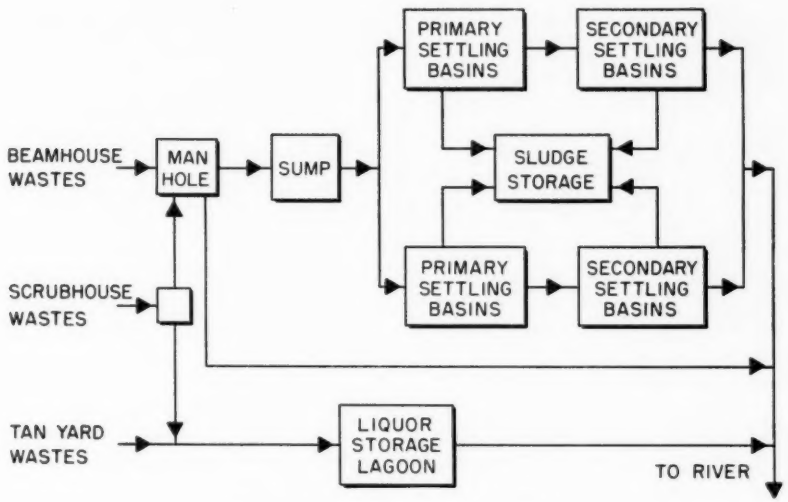


Diagram of Waste Treatment Plant
Vegetable Tan Process

In the following brief description, it is assumed that the tannery in question is located in a small community which has no municipal sewage disposal plant. The liquid wastes are all discharged into a nearby steam or creek. The accompanying diagram shows the flow of the liquid waste from the tannery to the receiving stream, after most of the solid material has been separated out by physical means such as mechanically cleaned bar racks. All the liquid effluents with the exception of the spent tan liquors and the soda bleach are mixed in a collecting sump which is usually a simple concrete basin equipped with paddle mixers operating at a slow speed. The mixed wastes then flow by gravity or are pumped to two primary settling basins which are arranged in parallel. In this first step, involving mixing and primary sedimentation, 80 to 90 per cent. of the suspended solids and possibly 40 to 50 per cent. of the B. O. D. are removed. The sludge, settled out in this primary sedimentation step, still containing approximately 90% water, is pumped or flows by gravity to the sludge storage area which is usually a low-lying waste area adjacent to the tannery. The effluents from the primary settling basins are conducted into secondary settling basins where the secondary sedimentation will take place. The sludge settled out in these basins is also removed to the sludge disposal area. The supernatent liquids from the secondary basins finally reach the receiving stream.

From the above diagram it can be seen that the spent tan liquors and the effluents from the soda bleach are not combined with the other liquid wastes,

but are conducted into an earthen storage lagoon where they are stored until they are discharged into the stream, as soon as the water level of the stream has reached sufficient height.

Wherever possible this procedure of storing the spent tan liquors should be followed as this particular portion of the effluent will sometimes represent almost half of the total B. O. D. of the tannery waste. Several attempts have been made in the past to evaporate the spent tan liquors, but this idea has been abandoned as it was found to be uneconomical. The dried sludge from the sludge storage is useful as a soil conditioner due to its high content of lime but so far little interest has been shown by farmers in the United States to utilize this material. No chemical settling agents, such as alum, are added to the wastes in the settling basins, as it has been found that the added efficiency of coagulation due to chemical treatment is too small to justify the increase in operating expense.

No dimensions of the actual size of the above disposal unit are given in this report, but the primary and the secondary sedimentation units are usually designed to provide 24 to 36 hours detention. They should be equipped with paddles for mixing during the period when wastes are entering the tank. Lagoons for storage of spent tan liquors and soda bleaches should provide about 325 U. S. gallons capacity per pound of hide per day. This comparatively large capacity of the lagoon is required, since its contents are only discharged into the stream when the water level is sufficiently high, which usually occurs only during early spring and late fall.

The cost of constructing and operating a treatment works, similar to the one shown in the diagram, will be dependent upon a number of factors. One of the most important of these is the topography of the land surrounding the tannery. If sufficient low lying land is available near the plant, then the sludge from the settling basins will not have to be pumped to the waste storage area where in all likelihood the storage lagoon for the spent tan liquors also will be located. Thus no pumps will be required for the removal of the above two waste materials.

Concrete settling basins are generally used for the primary and secondary sedimentation processes whereas earthen lagoons are in most cases quite satisfactory for the storage of the spent tan liquors. Depreciation of the concrete basins must be considered, but no depreciation allowance is usually made for earthen structures.

If a great deal of mechanical equipment, such as pumps, are used, then the services of one operator full time will be required. Otherwise the supervision of the disposal system can be entrusted to an employee on a part time basis. Additional labour will be required from time to time to keep the canals clean and in good repair. Concrete basins will necessitate a certain amount of repair work after some years, especially under adverse weather conditions and machinery such as pumps will have to be overhauled every year.

(*b*) *Discharge into a Municipal Sewage Plant*

The process briefly outlined above must be modified if the same tannery were located in a small town with a municipal sewage plant. In this case the tannery may discharge its waste directly to the sewage plant and the tannery effluent would be subsequently treated together with the municipal sewage. Certain precautionary measures must be taken by the tannery to ensure that the pH of the mixture obtained by mixing the tannery waste and the municipal waste should not be raised too much by the former, so as not to exert a harmful effect on the subsequent bacteriological digestion of the sewage. A municipal sewage plant operates at a pH level of no more than 8.5 and hence it may be required to lower the pH of the tannery waste by carbonation at the tannery itself or just prior to entering the municipal sewage plant.

(*c*) *Discharge into a Sewer System*

Should the same tannery be located in a large city, where the tannery would be discharging its waste into large municipal sewers, the pH value of the tannery effluent is lowered both by dilution with the municipal sewage and by carbon dioxide present in the sewers. Serious trouble may be experienced due to the formation of scale inside the sewers. This will be caused by the reaction of the lime present in the tannery waste and the carbon dioxide of the municipal sewage. In certain instances, scales of this type have been known to develop to a thickness of an inch in about a year's time. In order to avoid the formation of these calcium carbonate scales, the tannery wastes are often pre-treated by the tanneries before they reach the municipal sewers. The greater proportion of the lime and sodium sulfide in the tannery waste can be removed by primary sedimentation. Following this step the effluent is carbonated with flue gas or carbon dioxide, followed by secondary sedimentation to precipitate the calcium carbonate formed. As previously mentioned, the carbonation will also lower the pH of the tannery effluent thus avoiding any danger of interference with the subsequent biological treatment in the municipal sewer plant. However, if sulfides are present in large quantities in the tannery effluents, they can be precipitated with ferrous sulfate (Ferro-Floc) to form ferrous sulfide prior to primary sedimentation, in order to avoid the disagreeable odours of hydrogen sulfide formed when the pH of the tannery efflutent is lowered.

Some Possible Improvements in Equipment for Tanning Waste Disposal

In the not too distant future it may be feasible to reduce the cost of constructing a tannery waste treatment plant by certain improvements in design, even at the expense of a slight increase in annual operating costs. In this connection, reference is made to the possible use of common chemical en-

gineering unit processes and operations, such as filtration. Unfortunately no data are available as yet on the suitability of filters which would permit the recirculation of spent water. However, a certain amount of success in the reduction of B. O. D. and colour removal in the secondary treatment of tannery effluents has been achieved by using trickling and intermittent filters. Vacuum filtration has also been used to some extent in the United States to separate some of the water from the sludge settled out in the primary and secondary settling basins, but this method of separation has also been found to be rather expensive.

Mention should be made at this point of the recent process developed by Ionics Inc. of Boston, Mass., in which an attempt is made to separate the impurities from spent water by ion exchange. Adoption of the new device for a number of industrial purposes appears promising, but so far a solution has not yet been found for the problem of disposal of biological material, such as tannery wastes.

Regulations Governing the Disposal of Tannery Wastes

(*a*) *In the United States*

In the United States the individual states have the primary responsibilities and rights in controlling water pollution. In addition to the laws of the various states in the U. S. A. there is also the Federal Water Pollution Control Act (Public Law 845–80th Congress) which is designed to aid the individual states and interstate agencies through the U. S. Public Health Service and the Federal Works Administration in the formulation and execution of their stream improvement program.

Pennsylvania was one of the first states to introduce legislation pertaining to stream improvement. Following the example of this state, 45 out of the 48 states of the Union have now introduced legislation dealing with stream pollution. As early as 1923 the Sanitary Water Board of Pennsylvania was set up. This Board is composed of four members belonging to several government departments of the State and three non-government members. The Sanitary Water Board determines the required degree of treatment of sewage and industrial wastes based upon the local conditions. Therefore, in general, the wastes from a small tannery on a large river may require little treatment, unlike those from a large tannery on a small stream, where nearly complete purification may be necessary.

Systems of treatment have been devised involving various successive steps each providing an added degree of purification. The Board has set up three degrees of treatment in order to provide specifications for results to be obtained from industrial waste treating plants. They are the following:

(i) *Primary* treatment of industrial wastes comprising a treatment to a degree equivalent to that for municipal sewage. 35% of the organic pollution

load as measured by the B. O. D. test and all the settleable solids must be removed in this treatment.

(ii) *Complete* treatment which requires removal of 85% of the B. O. D. and complete removal of all the suspended solids.

(iii) *Intermediate* treatment which specifies treatments to varying degrees intermediate between primary and complete treatment.

The Water Board and the Public Health Department of the State of Pennsylvania co-operate very closely and see to it that the tanneries in their area comply with the specified standards. Shortly after the formation of the Water Board, the Tannery Waste Disposal Committee of Pennsylvania was formed which is composed of members of the tanning industry and representatives of the Water Board. The aims of this committee are to determine the characteristics of tannery wastes and the ability of streams to assimilate tannery wastes which have been treated to various degrees. The committee is also concerned with the study of treatment processes and the economic factors surrounding the waste treatment problem. Pennsylvania also has agreements on water pollution with bordering states through the agency of the Ohio River Valley Water Sanitation compact and other organizations.

(b) In Canada

In Canada we have the Federal Department of Health which amongst many other duties is concerned with the problem of water pollution on a nation-wide basis. Similar to the United States, the prime responsibility for controlling and administering the regulations concerning health and welfare rests with the authorities of the various provinces.

In Ontario the "Public Health Act" was passed in 1950, which regulates the supervision of health and contains rules aiming at the prevention or removal of conditions which are or may become injurious or dangerous to health. Amongst other things, the Act is concerned with all springs, wells, ponds, lakes, streams or rivers with reference to their purity. Polluting water by industrial wastes is deemed to be a nuisance within the meaning of this Act. Certain powers are conferred in the health authorities which consist in local boards, sanitary inspectors headed by the Chief Inspector of Health, the Department of Health and the Minister of Health and or his deputy. Penalties are provided for the enforcement of the decisions taken by the above mentioned authorities.

The establishment of so-called "offensive trades without the consent of the local board or of the municipal council constitutes an offence". "Tanning hides or skins" is mentioned in the list of "offensive trades".

The Act is well aware that existing unsanitary conditions, termed nuisances, e. g. pollution of water by wastes from industrial plants, established prior to the Act, cannot be removed all of a sudden and not without considerable cost.

Section 91 of this Act provides that no determination or order of the department or of a local board for the removal or abatement of a nuisance shall be enforced except by order of a judge of the Supreme Court, where such removal or abatement involves the loss or destruction of property to the value of $2,000 or more.

Comparing the Health Act of the State of Pennsylvania, Act 394, amended by Act 177, with the Ontario Health Act, it will be noted that the latter deals with water pollution only in general terms and abstains from establishing specific rules for the treatment of industrial wastes.

In addition to the Department of Health, another department, viz. the Department of Lands and Forests, is also concerned with the preservation of the purity of the watercourses. One of the many duties of this department is to ensure that the fish and wild life is not endangered through pollution of water.

Just this year the Pollution Control Board of Ontario was formed, composed of members of the Departments of Health, Lands and Forests, Planning and Development, Agriculture, Municipal Affairs and Mines. In addition, a proposal has now been made to form an Advisory Committee to the above Pollution Control Board. This committee would have representatives from the Health Officers' Association, Conservation Council of Ontario, Ontario Municipal Association, Canadian Manufacturers' Association, Chamber of Commerce, Ontario Association of Rural Municipalities, and there would also be on the committee consulting and municipal engineers, representatives from the universities and finally representatives from labour. This proves that the interest of the government in the problem of waste disposal is steadily growing.

Although the authorities, in framing the Health Act, have paid regard to the interests of both the public and the industrial user of water by refraining from drastic measures against the latter, it might perhaps be a sound policy for the tanners to enter into closest collaboration with the authorities with regard to the preservation of water purity. This end could perhaps be best achieved by the formation of a Tannery Waste Committee similar to the one set up in the State of Pennsylvania, composed of members of the tanning industry, representatives of the government and a number of experts.

Bibliography

Report of the Stream Pollution Committee. *Journal of the American Leather Chemists Association*, **45**, No. 1 (1950).

Camp, Thomas R. The Disposal of Tannery Wastes. Paper given at the New England Industrial Wastes Conference, June, 1950. *Journal of the American Leather Chemists Association*, **46**, No. 4 (1951).

A Condensed Report by the Tannery Waste Disposal Committee of Pennsylvania to the Sanitary Water Board on The Treatment of Tannery Wastes. October 8, 1930. *The Journal of the American Leather Chemists Association*, **26**, No. 2, (1931).

An Industrial Waste Guide to the Tannery Induxtry. Appendix "XI" of Supplement "D" to the Final Report to the Ohio River Committee. Federal Security Agency, U. S. Public Health Service. Office of Stream Sanitation, Cincinnati, Ohio, 1942.

Reuning, Howard T. Disposal of Vegetable Tanning Wastes. *Sewage Works Journal*, **20**, No. 3, May 1948.

Industry's Role in the Clean Streams Program in Pennsylvania. A Guide and Review issued by Pennsylvania State Chamber of Commerce, Bulletin 132, March 1950. Harrisburg, Pa.

Reuning, Howard T. Tannery Waste Treatment. *The Journal of the American Leather Chemists Association*, **42**, No. 11, (1947).

Reuning, Howard T. Tannery Waste Treatment. A Report by the Committee on Stream Pollution. *The Journal of The American Leather Chemists Association*, **38**, No. 8, (1943).

D. F. Maskey. A Study of Tannery Waste Disposal. I. Heavy Leather Beam House Effluents. *The Journal of the American Leather Chemists Association*, **36**, No. 3, (1941).

D. F. Maskey. Industrial Waste Disposal. "Hide and Leather and Shoes". February 10, 1940.

Industrial Wastes Bulletin No. 103. Department of Health, Bureau of Sanitary Engineering, Harrisburg, Pa., 1951.

Ontario Public Health Act, 1950.

The following persons were interviewed:

Howard T. Reuning, Keystone Tanning and Glue Company, Ridgway, Pa.
Dr. Richard Hoak, Mellon Institute of Research, Pittsburgh, Pa.
Mr. Carlson, The Mount Jewitt Tanning Company, Mount Jewitt, Pa.

APPENDIX

Equipment for Tannery Waste Treatment

Recently there has been a trend to minimize as much as possible the use of open lagoons and settling basins in order to shorten the process of disposal and also to avoid the odours and unhygienic conditions which result from the prolonged storage of putrefying waste liquids. Instead, various types of mechanical equipment have been developed to process the tannery wastes.

This report describes only some of the most commonly used types of machinery. Of course, the conditions vary in each tannery and each disposal set-up has to be adapted to meet a particular situation. In this brief paper only some of the salient features of the standard equipment are described and the units are dealt with in the same order as they would be found in a general flowsheet of waste disposal.

1. *Mechanical Screens*

These are generally used to remove coarse material found in the raw effluent, such as bits of string from the beam house or any large objects which

might damage pumps or any other units of the waste disposal plant. There are three kinds of mechanical screens on the market, namely, the revolving, the vibrating, and the bar type.

The bar screen has been found fairly satisfactory in many tanneries despite its inherent simplicity. This screen consists of a set of bars located in the flow channel, set at an angle of 60 degrees to the flow. The spaces between the bars vary from ½" to 2". The objects retained by the bars can be removed either by mechanical or manual means.

2. *Fine Screens*

These screens are distinguished from mechanical screens, in that the openings range from 1/16" to approximately 1/4" in size. They are used to intercept finer solids than the mechanical screens can catch, and are useful in the removal of hair from the beam house effluents. There are two types of fine screens, namely, revolving drums, and revolving discs. Both types are covered with perforated metal plates. The perforations of the plates are kept clean either by a set of revolving brushes which travel along the tip of the screen as it revolves, or by jets of water.

3. *Sedimentation or Settling Units*

In any tannery treatment plant some type of sedimentation unit will be necessary to bring down the bulk of the settleable solids in a reasonable period of time, normally considered to be from two to four hours. In order to have a continuous and fast process, mechanically cleaned clarifying tanks are employed in preference to the simple batch process employing open settling basins for sedimentation.

There are two general forms of mechanically cleaned tanks,

1. The circular tank with revolving sludge collecting mechanism, or
2. The rectangular tank which has a length equal to several times its width.

A circular tank is fitted with a mechanism consisting of a central shaft or column to which arms are attached equipped with scraper blades which pass close to the bottom of the tank to collect the settled material. These units are driven by means of a motor located at the centre of the unit on a supporting superstructure which revolves the central shaft or column through a train of gears usually enclosed in an oil bath. The method of feeding these tanks is either from the centre upwards through a hollow central column or pier from which the flow radiates outward through a weir around the central periphery, or from a central feed well, fed by a pipe brought in under the liquid level from the side of the tank.

The rectangular type of tank is equipped with a mechanism composed of a chain running over sprockets located at the bottom and top of each end of the tank and driven by a motor located at the top of the tank, through

another set of chains and sprockets. Rakes are attached to the chains and the sludge which settles out at the bottom is moved to the end of the tank where it is collected in a sludge pocket.

Sedimentation is usually carried out in two stages, i. e., primary and secondary sedimentation. Therefore at least two vessels are required for these operations. Both the circular and the rectangular tanks are in use and the preference given either one of the two will depend on the amount of space available (the rectangular tank needs less space) and personal considerations which may favour one or the other type of mechanism.

It should be mentioned that the batch process of sedimentation requires a much lower investment than the process employing mechanical sedimentation methods. It has been found that the batch process is still fairly satisfactory for tanneries located in rural areas where sufficient waste land is available and where the odours do not give rise to serious complaints from residents.

4. *Sludge Pumps*

To remove the settled solids from sedimentation tanks, it is necessary to provide pumps. The piston or plunger displacement-type pump is commonly found very satisfactory for pumping this type of material. As it is necessary to remove the sludge from the tank at the same rate as it is deposited, and since the rate of settlement will vary from time to time, it may be advisable to instal a plunger type of pump with an adjustable stroke.

5. *Pumps for the Disposal of the Final Effluent.*

The overflow from the secondary sedimentation tanks is at this point sufficiently conditioned to be disposed of either by force of gravity or by pumping. In the latter case centrifugal pumps are commonly used with an "open-type impeller". It is good practice to install at least two pumps for this purpose, so that if trouble occurs with one pump, the other will be available for service.

In selecting waste treatment equipment one should try to achieve the following advantages:

1. Low initial, over-all, and completely erected cost.
2. Least cost in operation, from the standpoint of power consumption and repairs or replacements due to wear.
3. Reputation of the manufacturer and reliability of the service organization.
4. Accessibility for repairs without requiring the emptying of tanks or basins.
5. Simplicity of construction.
6. Efficiency of performance, in percentage of results obtained.
7. Suitability for the available site.
8. Compactness (adaptability to adjacent units)
9. Protective devices.

Catalogues and brochures describing the equipment used in tannery waste disposal are on file at the Ontario Research Foundation.

Bibliography

Industrial Waste Treatment by E. B. Besselievre.

Knowles, C. L., Industrial Wastes from the Equipment Manufacturers' Viewpoint, *Industrial and Engineering Chemistry*, **31**, 1338 (1939).

Instrumentation for Waste Treatment, Bulletin 7301, Brown Instrument Company, Philadelphia, Pa.

Process Manual of the Dorr Company Inc., Stamford, Conn.

Received February 27, 1953

ABSTRACTS

Modern Practice in Leather Finishing. III. By W. O. Nutt. *Leather Trades Rev.* **103**, 133 (1952). The first consideration in any finish formulation is the result desired. The nature of the leather, the application methods, drying conditions, and any subsequent operations must also be taken into account when formulating a finish, hence only general directions are in order. In a protein glazing finish, no appreciable grain covering can be effected, and skins must be selected for good grain. Pigments should be in paste form and very finely ground. Glazing itself is largely a matter of friction. The glass passing over the finished leather creates enough heat by friction to soften the finish so that it levels readily. Too great heat is harmful to unstable colors, so for this reason lake colors are not very suitable for glazing finishes. Also, pigment pastes fortified with particularly volatile dyestuffs may give a streaky effect from the same cause. Plasticizers in the casein film should be stable up to 150°C., which qualification eliminates sulfonated oils, but does not exclude the glycol type materials. A good quality glazing pigment finish should deposit a film consisting of approximately equal parts of dry color and dry plasticized casein, and the seasoning coat should be casein solution slightly less plasticized with a 6 per cent solids content. It should contain about 12.5 per cent of 40 per cent formaldehyde. One coat each of the base pigment and glazing season top coat should suffice. Another practice is to use a hard acrylic resin undercoat with a glazing pigment applied on top prior to glazing. Many manufacturers add water soluble dyestuffs to their glazing finishes, especially for chromes, for the purpose of attaining clarity of color associated with glazed leathers, but this practice is not as satisfactory as the use of synthetic precipitated dyestuff as the only coloring material, used in conjunction with a good wetting agent. Anionic wetting agents are the most satisfactory. While the resistance to wet rubbing of a formalized casein is quite good, it may be improved by a spray coat of 2 per cent formaldehyde solution. If still greater fixation is desired, glyoxal can be used. An ordinary finish differs from a glazing finish in that the latter contains a larger percentage of color and plasticizer. Shellac, albumen and waxes are used as replacement materials for casein. Pigments may be powder or paste. Powder pigments should be thoroughly dispersed in water, usually with the addition of a small amount of ammonia. An ordinary finish film should consist of one part pigment to two of binder. Two thin coats are to be preferred to one heavy one, with the first one thickened with one of the cellulose derivatives. Finishes are usually fixed to wet rubbing by formaldehyde solutions, but where a high per-

centage of cellulose derivative is present, shellac or wax dispersions prove advantageous. On the other hand, acrylic resins find favor as fixatives.

The French Tanning Extract Industry. *Leather Trades Rev.* **103,** 136 (1952). France produces about 13,000 metric tons of pure chestnut and oak tannins. One of the important uses of these materials is for boiler water treatment by the French National Railway Company, however, enough is being produced to allow some export business. Prior to 1914 practically all extract was in liquid form, but the powdered material is gaining in favor. Because of the shrinkage of the chestnut forests much attention is now being given to reforestation and efforts to decrease the effects of tree diseases.

Vegetable Tanned Belting Leather. British Processes for Producing the Best Quality. *Leather Trades Rev.* **104,** 567 (1952). The best type of oxhide is essential, with English, North Italian and Swiss preferred. Hides are given a short soaking in plain water in a slowly revolving drum. Liming is by the 3-pit suspension method, and rocking of the hides for 7-8 days. The stock is then unhaired, fleshed, scudded and rounded, at which point hides unsuitable for belting leather are routed to sole leather. The belly trim is square, without taper, and shoulders are cut off at a maximum length of 4.5 feet from the root of the tail. Hides are delimed with boric acid or sodium bisulfite, but are not bated. Deliming is usually about two thirds through the hide as determined by Phenolphthalein. Tannage is begun in 15°Bk. liquors of 4.5 pH, consisting of a fair percentage of myrobalams. Tannage is completed in liquors of 100°Bk. and 3.7 pH, and requires at least a month in layers. Usually the tanner sells the butts in the rough to the currier. Here the leather is soaked back until it is soft and pliable, after which it is shaved or skived to remove excess flesh. Both grain and flesh are scoured on a flat table to remove excess surface tannin. Stock is then sammied for hand or drum stuffing, with the former preferred. Raw cod is applied to the flesh and dubbin applied to the grain. The dubbin is made of equal parts of cod and tallow. The leather is then partially dried, the excess dubbin scraped off, stock set on on the flat table setting out machine, then stretched to dry. When removed from the stretchers the leather is given a light application of dubbin or tallow and piled to mature or age. After this, grease is slicked off, a soap size applied to the flesh side and the leather jacket and brushed.

Fine Art of the Sole Leather Tanner. X. Durio Drum Tannage. By W. Petrie. *Leather Trades Rev.* **105,** 63 (1952). Lime sulfided hides are thoroughly delimed with sodium bisulfite in drums, given the usual beam house treatment, and suspended 4 days in fresh liquors of about 30°Bk., well bisulfited, and containing a sufficiency of acid. After this time they are set enough for drum tanning. After 4 packs have been through the suspender liquors, these liquors are set aside for the tanning of upper leather. The drum liquors are of the same composition as the suspender liquors but are allowed to mellow through continued use. Their Bk. is usually 80°. Advantages of the system are, lessening of the time of tannage, employment of higher temperatures (drum temperature rising from 65 to 90°F.), decreased manpower, little waste of tanning material, small volume of liquor. Disadvantages are, liability of stock to become over heated in the drum through insufficient liquor, rubbing, pebbling if grain is not properly preset, leather weight and substance usually lacking, and greater power and upkeep costs. There are no straight sole leather drum tannages in Britain at the present time, but drums are used to hasten tannage in various stages of the tanning operation.

Practical Color Matching of Leather. By B. Barratt. *Leather Trades Rev.* **105,** 318 (1952). Use of basic, and chrome mordant, and molan dyes in the dyeing of leathers is discussed.

German Experiments to End Warble Fly. *Leather Trades Rev.* **105,** 477 (1952). Larvae which have reached a progressed development and which show a plain brown coloring of the epidermis are not killed with concentrated Derris emulsions. They can be killed by cyanic acid, phenol, cyanamid, nitrogen and sulfur dioxide, or suffocated by painting the openings with acetone-cellulose cement. The paint lasts about 6 weeks and is very effective, killing larvae at every stage. The material is easily applied by any layman and is relatively cheap.

The Acid Hemlock Tannage Has Gone But Lessons May Be Learned from an Old Time Process. By W. Petrie. *Leather Trades Rev.* **106,** 667 (1952). Acid hemlock leather was made from sweated hides which were first thrown into cold water, hand fleshed and unhaired, colored for about 15 minutes in a lattice drum containing a weak 14°Bk. hemlock liquor, then hung over sticks for two days in pools of sulfuric acid water. They were then immersed in very weak liquors, which became progressively stronger until the last was about 70°Bk. The coloring liquors contained well under one per cent tan, and were the oldest in the tan yard. The first liquor of the tanning proper was about 20°Bk., and high in nontans. Tannage progressed very evenly, with a very definite white streak between the tanned and untanned portions. Correctess of the tannage was judged by the appearance of this streak. If the streak was not as prominent as the tanner wished, he would fear a harsh leather. Hides kept too long in the acid water, or if the waters were too strongly acid, this condition would obtain. Reuse of the weakest tan liquor proper also caused harshness. Evidently the hides were very plump at or near the moments throughout the tannage when the tans came into contact with the untanned parts of the hide. The leather bore the marks of high tannin fixation, and this observation coincides with the modern concept of tan fixation being associated with hide plumpness. Another observation to be made from the acid hemlock process is that hide may enter a low pH liquor and finish out in a higher pH liquor, yet remain plump. Another conclusion is that hides can be well plumped without detriment to the fiber, and finally, an alkaline plumping prior to tanning is unnecessary.

Determination of Free and Total Acidity in Commercial Lactic Acid. By W. R. Fetzer and R. C. Jones. *Anal. Chem.* **24,** 835 (1952). Disagreements between laboratories on the determination of free and total acidity in commercial lactic acid prompted an investigation of the various methods given in the literature. No standard or universally accepted method was found. A new titrametric method calls for an excess of standard alkali over the required for free acidity with a retention time to effect the hydrolysis of the anhydride. The amounts of excess alkali and the required holding time are determined experimentally. The method has been in use for five years and has given good agreement between laboratories.

Homogeneous Precipitation of Barium Sulfate by Hydrolysis of Sulfamic Acid. By W. F. Wagner and J. A. Wuellner. *Anal. Chem.* **24,** 1031 (1952). The determination of barium through the homogeneous precipitation of barium sulfate by the slow hydrolysis of sulfamic acid gives excellent results. This method yields coarse crystals which are

more easily filtered and washed free of absorbed ions than those obtained by the standard sulfuric acid procedure. Several foreign ions, particularly calcium and iron, cause little interference. Strontium, in all but trace amounts, interferes.

Maintenance and Care of Belt, Chain and Gear Drives. By J. deFeber. *Shoes and Leather*, **24,** No. 6, 18 (1952). In the case of flat belts, incorrect alignment of pulleys and belts, vibration, slippage and slackness, and surrounding dust and dirt are causes of trouble. Belts should be installed so that the slack side is on top of the pulleys and the pulling side is on the bottom. They should be run with the least possible tension at maximum load without slipping. Belts will become glazed or have dry surfaces if they are operated over crowns which are too high. If they are stretched unduly on one side, or if the ends are not squarely joined, they will run crooked. Undue wear on the edges is usually caused by belt guards, guides, or pulley flanges. Dirty belts should never be cleaned with wire brush but rather with fiber brush or soft rubber strip. They should not be treated with sticky, gummy dressings. Belts should be stored in a dark, cool place in an atmosphere which has little steam or moisture.

On the Molecular State of Water Bound to the Peptide Linkage. By M. Tsuboi. *Bull. Chem. Soc. Japan* **25,** 160 (1952). In order to obtain information about the molecular state of water bound exclusively to the peptide linkage the author made 3μ region infrared absorption measurements of a film of amilan [. . .— $CH_2)_5$ – CONH – $(CH_2)_5$ – CONH —] in dry as well as in wet state and found that there exists a band at about 2.86μ which is attributable to the water bound to the peptide linkage in this compound. Bound water of gelatin and other proteins always show absorptions not only in 2.85μ - 2.90μ region but also in 2.90μ - 3.03μ region. Amilan bound water shows none in the 2.90μ - 3.03μ region. This is taken to indicate that the water molecules which cause the absorption in the 2.90μ - 3.03μ region are those bound to the side chains of the proteins, and those bound to the peptide linkages cause the absorption at about 2.86μ. The O-H band of amilan-bound water or peptide bound water is situated at a wave length much shorter than the O-H band of pure water (at 2.95μ), indicating that the water molecule in peptide linkage is in a less distorted state than the water molecule in pure water.

The Combination of Wool with Acids. By W. Harrison. *J. Soc. Dyers and Colourists* **68,** 176 (1952). After discussing a number of mathematical formulae which have been devised to express the quantitative absorption of acid and acid dyes by wool, the author suggests still another. He offers a series of curves, plotted from calculations made according to the proposed and other formulae, which show generally close agreement with one another.

A Century of Colorimetry. By M. G. Mellon. *Anal. Chem.* **24,** 924 (1952). A review of the subject with 128 references.

Iodometric Determination of Copper. By L. Meites. *Anal. Chem.* **24,** 1618 (1952). Procedure:—Evaporate a nitric acid solution containing not more than 150 mg. of copper nearly to dryness, add 3 ml. of concentrated sulfuric acid, and evaporate to incipient dryness. Repeat the second evaporation if the residue is large and nitrate may still be present. (Evaporation with sulfuric acid would give the slowly soluble anhydrous sulfates of iron

and chromium, which might retain some copper and would have to be redissolved in hydrobromic acid. To avoid this, perchloric acid may be used instead of sulfuric acid if chromium is known to be absent. Perchloric acid may be used even in the presence of chromium if the chromate produced is removed with barium chloride or if the result is corrected for the amount of chromium present. Dissolve the residue in 25 ml. of water and add 1 gram of sodium acteate, 4 grams of sodium fluoride (unless tin and iron are known to be absent), and 25 grams of potassium iodide. Swirl for 10 to 15 seconds, then titrate with 0.05 to 0.1 N thiosulfate. Starch indicator may be added near the end of the titration if desired: it is unnecessary with pure solutions of copper salts. There is no need to standardize the thiosulfate against copper, for the titration is stoichiometrically exact. If the weight of copper present is greater than 150 mg., either the amount of potassium iodide or the concentration of the thiosulfate must be increased to prevent precipitation of copper iodide.

Determination of Moisture in Oils and Greases. By R. Y. Mulheim and U. N. Roark. *Anal. Chem.* **25,** 348 (1953). The authors describe equipment and procedure for the determination of moisture in oils and greases, using the toluene distillation technique. The refinements introduced include an efficient fractionation column, a method of heating the column, tubes and condenser, and a better azeotrope former. It is claimed that highly accurate and reproducible results are obtainable at less time.

Recommended Specifications for Reagent Chemicals. By E. Wichers. Chairman A.C.S. Com. *Anal. Chem.* **25,** 36 (1953). This report contains recommended specifications for ten reagent chemicals not included in the book, "Reagent Chemicals, American Chemical Society Specifications, 1950," and a considerable number of recommended changes in the specifications published in that book. The committee will recommend to the Council of the Society at its meeting in March 1953 that these new specifications and revisions of previously published specifications be officially approved in the same manner as the text of the above-mentioned book was approved on April 10, 1950. If so approved, the complete specifications contained herein will be considered to be official specifications of the American Chemical Society, effective from July 1, 1953, and the partial ones will be similarly considered to constitute official revisions of the pertinent parts of specifications previously approved by the Society. The material in this report should be regarded as an appendix to the 1950 volume, whose introductory text relating to Definitions, Procedures, and Standards should be consulted for general information on the interpretation of requirements and on the conduct of methods of test.

Coatings. By R. W. Stafford and J. F. Shay. *Anal. Chem.* **25,** 8 (1953). This review covers chemical and physical analytical methods applicable to organic high polymers and associated oils, waxes, pigments, and plasticizers as reported in the literature during 1952. One hundred thirty eight references are cited.

Water. By S. K. Love and L. I. Thatcher. *Anal. Chem.* **25,** 65 (1953). This is the fifth of annual reviews of analytical methods used in water analysis. 183 references are given.

Titration of Sulfates. By O. I. Milner. *Anal. Chem.* **24,** 1247 (1952). The gravimetric determination of small amounts of sulfate is subject to considerable error. Where the sulfate is in the form of sulfuric acid, it may be determined by titration with standard base, but other acidic components interfere. To provide an alternative to titration with barium chloride conductometrically or with tetrahydroxyquinone as an indicator, a high frequency oscillator has been adapted to the determination. The method is based on the titration of the sulfate using a titrator of the tuned-plate tuned-grid type. The instrument and titration technique are suitable for the determination of sulfate in aqueous solutions containing a few tenths of a milligram of sulfate.

Electron-Microscopic Investigation of the Effect of Electrolytes on the Structure of Collagen. By A. L. Zaydes and S. L. Pupko. *Doklady Akad. Nauk. S.S,S,R.* **80,** 647 (1951). Through *J. Soc. Dyers and Colourists* **68,** 231 (1952). Collagen is treated with solutions of acetic acid, hydrochloric acid, ammonium sulfate, and ammonius thiocyanate, and the changes in structure are observed by means of the electron microscope. Both acetic and hydrochloric acids at 0.01 N lead to the breakdown of the fibrils into subfibrils, which are found to be in the form of an intricate network. At normal strength, acetic acid causes an apparent loss in structure, while HCl leaves the original fibrillar structure apparently unchanged. These results are in accord with the increased swelling in acetic acid with increase in concentration, and with the reverse effect for HCl. Ammonium sulfate produces a loosening and opening up of the fibrillar structure, while ammonium thiocyanate causes a compacting of the structure with loss of the original striped appearance.

Thin Membrane in the Surface Layers of Human Skin and Finger Nails. By G. Lagermalm, B. Philip, and J. Lindberg. *Nature* **168,** 1080 (1951). Through *J. Soc. Dyers and Colourists* **68,** 231 (1952). Thin pieces of skin loosened from sun-burnt human back, thickened skin from the palm of the hand, and finger-nail parings are treated for 6 days at 50°C. and 14 days at room temperature with 1 per cent NaS. Electron micrographs of the washed and palladium-shaded residues show membranes wrinkled to a much higher degree than those from hairs and feathers, with wrinkles running in all directions. This may be due to the membranes having originally enclosed ellipsoidal cell structures rather than cylindrical structures. Wool epicuticle shows signs of damage after treatment with hyaluronidase, but if wool itself is so treated no increase in acid sorption is found.

The Chemistry of Chrome Tanning. By P. K. Sarkar. *Leather Manufacturer* **63,** No. 10, 7 (1952). A discussion of one bath chrome tanning.

Note on the Action of Nickelammonium Hydroxide on Proteins in General. By J. W. Bell and C. S. Whewell. *J. Soc. Dyers and Colourists* **68,** 395 (1952). Nickelammonium hydroxide combines not only with wool, but also with feather keratin, hide powder, egg albumen, casein, and formalised casein. Some proteins dissolve yielding red solutions, from which metal-containing complexes may be obtained by addition of ethyl alcohol. The nickel content of these complexes is high. Polyglycine is soluble in concentrated solutions of nickelammonium hydroxide.

Shrinkage of Dry Collagen. By G. I. Kutyanin. *Doklady Akad. Nauk S.S.S.R.* **82,** 405, (1952). Through *J. Soc. Dyers and Colourists* **68,** 331 (1952). Collagen—(a) un-

tanned, (b) tanned with a vegetable extract, and (c) tanned with chrome—is allowed to shrink in the wet and in the dry condition under the action of heat. The wet collagens give shrinkage temperatures of (a) 70, (b) 80 and (c) 120°C. The dry collagens also show shrinkage effects. Their length-temperature curves are very similar, showing a rapid fall at ~ 110°C., followed by a gradual fall to ~ 210°C., when a final rapid fall sets in. However, the temperatures for complete shrinkage vary—(a) 220, (b) 250, and (c) 260°C. The observations are interpreted in terms of the effect of heat and water on the intermolecular forces and linkages present in tanned and untanned collagen.

Industrial Exposure to Chromates in New York State. By H. S. Dankman. *Arch. Ind. Hyg. Occupational Med.* **5,** 228 (1952). Through *Chem. Abst.* **46,** 10488 (1952). Workers incur exposures to Na_2CrO_4 and $Na_2Cr_2O_7$ in chromate manufacture, to $ZnCrO_4$ in pigment manufacture, to H_2CrO_4 in anodizing and plating operations, to $Na_2Cr_2O_7$ and $Cr_2(SO_4)_3$ in leather tanning, and to $(NH_4)_2Cr_2O_7$ in photoengraving.

Tanning of Fatty Acid and Protein Monolayers by Metal Ions (Chromium, Aluminum, Iron and Copper). By J. H. Schulman and M. Z. Dogan. *Nature* **170,** 31 (1952). Through *Chem. Abst.* **46,** 10653 (1952). The similarity of the reaction of these ions with fatty acids to their reaction with proteins is pointed out. Both reactions involved carboxyl groups.

The Use of Petroleum Sulfonates (Synthane) as a Leather Tanning Principle. By A. I. Angelopulo. *Legkaya Prom* **10,** No. 1, 28 (1950). Through *Chem. Abst.* **47,** 10653 (1952). Experiments are reported on the production of tanning principles from acid tar, which is formed in the purification of paraffin, and from the polymerized residues from the second gasoline distillation. These products are converted into sulfonic acids by 5-fold sulfonation. The sulfonic acids so formed are converted into Na or Ca salts and the salt solutions are concentrated to a density of 1.06. The Na salts are superior to the Ca salts for hard leather tanning. The sulfonates obtained from the byproducts of the purification of paraffins are superior to those from the polymerized products.

The Rapid Polarographic Determination of Sugars in Extracts of Tanning Materials. By J. Dlezek. *Sbornik Mezinarod. Polarog. Djezdu Praze*, 1st Cong. 1951, Pt. I, *Proc.* 736. Through *Chem. Abst.* **46,** 11731 (1952). To 50 ml. of the extract and to another 50 ml. to which has been added 0.01 – 0.015 g. glucose and 5 ml. saturated basic lead acetate solution and filter. Precipitate the lead in 30 ml. of the filtrate with 5 ml. saturated Na_2HPO_4 solution and filter again. To 10 ml. of the second filtrate add 0.6 - 1.3 ml. (depending on the quantity of sugar) Fehling I and II solutions and boil for 5 minutes. Cool the solution, add 0.01 per cent gelatin, make up with water to 50 ml. and filter. To 5 ml. of the filtrate add 3 ml. concentrated NH_4OH and polarograph. Determine the sugar content by decrease in the Cu wave.

Preservation of Leather by Means of Lanolin. By K. R. Stüdemann. *Seifen-Ole-Fette-Wachse* **77,** 461 (1951). Through *Chem. Abst.* **46,** 11736 (1952). Solutions of lanolin (maximum 30 per cent) in mixtures of benzene and turpentine are good preservatives for leather articles including transmission belts.

Leather and Tanning Agents III. Tanning Experiments with Polyamides. Theory of Tanning. By H. Batzer and G. Weissenberger. *Macromol. Chem.* **7,** 320 (1951). Through *Chem. Abst.* **47,** 901 (1953). The absorption of quebracho tannin by Igamide 6 A (polyamide condensed from 60 per cent hexamethylene diamine and adipic acid and 40 per cent caprolactam), collagen, and skin powder is measured. On the basis of N content, which is proportional to the amide group concentration, the tannin is taken up in identical amounts. Since the tannin can be completely removed, it is not bound by primary valence bonds but rather by absorption at the peptide link. The tanning thus represents a dehydrating plastification of collagen, the "plasticizing" water in collagen being replaced by the tannin.

Tanning and Detanning of Elastin and Collagen Fibers. IV. By H. Batzer and G. Petry. *Macromol. Chem.* **7,** 328 (1951). Through *Chem. Abst.* **47,** 901 (1953). Complete removal of the tanning agent regenerates the physical properties of the starting material. The removal of quebracho tannin is followed by stress-strain curves. The data are interpreted on the basis of the theory of dehydrating plastification of the tanning process.

The Aldehydes Existing in Gelatin. By J. Pourader and A. M. Venet. *Bull. Soc. Chim. Franc.* **347,** (1952). 2-Thiobarbituric acid, 1 g. in 180 cc. glacial acetic acid, and 20 cc. H_2O were mixed with gelatin at room temperature for 6-16 hours; then the mixture was heated on the water bath for 15 minutes and diluted with water. Both acid- and lime-cured gelatins of different origin yielded brownish yellow to rose colorations. The spectra of the solutions showed maximum absorption at 450μ in each case. The authors postulate the presence of two unidentified aldehydes in gelatin irrespective of origin or preparation.

Fatliquoring Leather with Pastol. By S. A. Kuraitis. *Legkaya Prom* **10,** No. 1, 24 (1950). Through *Chem. Abst.* **47,** 1417 (1953). Emulsions of Pastol (I), a petroleum base product, or of I with fatliquoring compounds are sufficiently stable. Fatliquors of mineral origin are emulsified readily with I. At 20°, it is absorbed rather weakly by the hide substance; in the presence of leather oil and a small amount of castor oil absorption is better. In fatliquoring chromed material, absorption of I increases sharply to 5 per cent of the weight of the leather. Chromed material absorbs best mixtures of I with leather oil and I with sulfonated fish oil. In the presence of I, absorption of oak extract tannins is normal. The coefficient of tanning is even higher than without I. Additions of I in vegetable tanning should be studied to determine I dosage and establish the best time of addition (in the first or second tanning phase).

Tanning of Leather with Oak Extracts in the Presence of Pastol. By S. A. Kuraitis, *Legkaya Prom* **11,** No. 1, 42 (1951). Through *Chem. Abst.* **47,** 1418 (1953). Satisfactory results were obtained in tanning chromed Russian leather with oak extract in the presence of the fatliquoring agent "Pastol". Emulsions formed by Pastol (up to 50 per cent) and sulfonated fish oil were especially stable.

X-Ray Diffraction Studies of Leather. By S. D. Bailey and V. F. Albert. *Proc. Iowa Acad. Sci.* **59,** 344 (1952). Through *Chem. Abst.* **47,** 3019 (1953). The x-ray diffraction pattern of russet-dyed leather consists of reflection arcs due to pigments, stuffing greases, and the spacings of the collagen polypeptide chain. Where changes resulting from the deterioration of leather involve these substances, x-ray diffraction will prove a quali-

tative method for its evaluation. No reflection arcs have been observed for the tanning agents, though three arcs have yet to be accounted for. A comparison of new and deteriorated leathers by x-ray diffraction is being presently investigated.

The Sulfite Waste Liquor Tanning II. Absorption of the Mixture Consisting of Sulfite Waste Liquor Tanning Agents and Natural Tannins by Hide. By Y. Hachihama and Y. Kyozoku. *J. Chem. Soc. Japan* Ind. Chem. Sect. **54,** 227 (1951), Through *Chem. Abst.* **47,** 3016 (1953). Pelts, limed as well as delimed, and hide powder were tanned with liquors consisting of sulfite waste liquor and natural tannin in various proportions, and the changes of the components of the liquors with time were studied. The natural tannin was absorbed to a greater extent than lignin sulfonic acid.

Reaction of Tanning Compounds with Polyamides. By I. P. Strakhov. *Legkaya Prom* **10,** No. 2, 25 (1950). Through *Chem. Abst.* **47,** 3017 (1953). Caprolactam polyamide fibers were tanned with oak tannins and also with chrome compounds of different compounds and charge. Some fibers were treated with phenol prior to chrome tanning. Only the tannins react with the peptide groups of the polyamides. Preliminary treatment of fibers with phenol resulted in a sharp increase of absorbed organic compounds from the tannins.

Action of Trypsin, Pepsin, "Concentrate", and Oryzone on Collagen and Hide. By I. S. Shestakova, *Legkaya Prom* **9,** No. 7, 23 (1949). Through *Chem. Abst.* **47,** 3019 (1953). The effect of trypsin, pepsin, "concentrate" (an enzymic preparation not further described), and oryzone is determined chiefly by the preliminary treatment of the collagen. Within the limits of the same substrate, trypsin, "concentrate", and oryzone give approximately the same decomposition values. Under the action of oryzone on collagen treated with alcohol, the solubilization was greater with "concentrate" and trypsin. For hides delimed and softened with "concentrate" and oryzone, the solubilization was less with oryzone than with "concentrate", trypsin and pepsin; upon subsequent treatment with trypsin, pepsin, "Concentrate", or oryzone, the solubilization of hide softened with oryzone increased sharply in comparison with that softened with "concentrate". "Concentrate" and oryzone seem to act differently on collagen and hide. Oryzone seems to produce the primary, not final, effect.

Characteristics of Sheepskin Dyeing. By K. A. Krasnov. *Legkaya Prom.* **10,** No. 3, 12 (1950). Through *Chem. Abst.* **47,** 3597 (1953). An attempt to dip dye sheepskin with a mixture of naphthol blue-black 65, acid orange 30, and Bordeaux AT 5 per cent resulted in different colorations of skin and wool. It is explained, on the basis of molecular weights and colloidal and physical characteristics of these dyes, that this is caused by differential extraction of these dyes from solution.

Shrinkage and Heat Resistance of Leather Innersoles. By N. I. Punenkov, A. S. benko, and K V. Rykberg. *Legkaya Prom.* **10,** No. 5, 28 (1950). Through *Chem. Abst.* **47,** 3597 (1953). Water solubles play a decisive role in the shrinkage process, and fixed tannins come next. Shrinkage was reduced from 2.9 to 0.7 per cent by filling. Heat resistance was also raised. For rigid conditions of hot vulcanization, shrinkage should not exceed 0.9 per cent. For less rigid conditions, as for shoes with coarse uppers and thick soles, it may be as high as 1.3 per cent.

pH of Tannins During Tanning of Sole Leather. By S. V. Gerasev, M. P. Zhurbenko, and K. V. Rykberg. *Legkaya Prom.* **10,** No. 5, 28 (1950). Through *Chem. Abst.* **47,** 3598 (1953). Mixing of oak with AN syntan resulted in increase of tannins, but addition of Na_2SO_3 to raise the pH to 4.4 caused a loss of tannins, and gave a lower leather yield with regard to weight and thickness.

The Analysis of Synthetic Tannins. By P. Chambard and A. Jamet. *Bull. Assoc. Franc. Chim. Inds. Cuir* **12,** 167 (1950). (See also *ibid.* **12,** 72 (1950). Studies were made on five synthetic tannins to determine what conditions of temperature and time of agitation would give the same figure for tannin by the shake method as is obtained by the filter-bell method at 18°C. The effect of time is not too marked, but 30 mins is suggested as the optimum. Increase in temperature increases the tannin found up to about 30° - 35°C, beyond which point further increases result in a fall-off in tannin due to increased non-tans arising from hydrolysis of the hide powder. Even at such optima, the two methods only agreed on one syntan. It is concluded that the analysis of an unknown synthetic tannin should always be preceded by a tanning test and a determination of pH, and that the so-called auxiliary tannins, which are devoid of leathering powers and are very acid, should not be submitted to tannin analysis. A.N.K.

Corrosion Resistance of Metals, Alloys and Stainless Steels. *Bull. Assoc. Franc. Chim. Inds. Cuir* **12,** 173 (1950). By P. Chambard and F. Abadie. Plates of Pure Ni (I) Monel, (II) Inconel, (III) Stainless Steel No. 1, (IV) Stainless Steel No. 2, (V) were submitted to the action of 4° Be′ liquors of powdered, ordinary Chestnut: a syntan used in iron-tannage; a replacement syntan. The test was run for a total of 12 days at 100°C. for each extract; with chestnut, a second series were tested by autoclaving to 120°C. for 1½ hours each day for the 12 days. While the ratio of the liquor-metal was very much less than would obtain in industrial autoclaves, it is felt the results are at least relative. The loss in weight of the plates (mg/cm_2) their appearance and the nature of the deposits formed were noted; the liquors, after test, were observed colorimetrically (Lovibond Tintometer and photocolorimeter) and changes in pH and iron-content determined. Finally, the liquors were used to tan pieces of skin and the appearance and color of these was observed. In general, I and II were the more rapidly corroded. In all cases, the liquors darkened considerably and the leathers showed similar color changes compared with freshly-papered controls. The pH of the test-liquors increased and the increase was roughly in agreement with the corrosion rate. The composition of IV and V is not given. A.N.K.

Study on the Tannin of the Bark of Eucalyptus Sideroxylon. By P. Chambard and F. Abadie. *Bull. Assoc. Franc. Chim. Inds. Cuir* **12,** 193 (1950). The second of two parts (see *ibid*, June, 1950). Studies were made of treatment with sodium sulfite and bisulfite. When the ground bark was extracted with solutions of these salts, bisulfite gave greater reduction in insolubles but increased nontannin; sulfite gave a higher ratio of tans to nontans and a greater lowering of viscosity. Tannage of pieces of delimed calfskin showed that a 0.25 per cent bisulfite solution was the minimum for improvement in color and speeded penetration; neither sulfite nor a 50/50 mixture of sulfite and bisulfite improved either the color or speeded penetration. The ordinary extract of the bark was then treated for 2 hours with bisulfite (1) on the steambath, (2) in the autoclave at 130°C: prepared as (1), color and viscosity fell while the rate of penetration increased as the amount of bisulfite was increased up to 4.5 per cent on the dry basis; prepared as (2), viscosity fell only slowly while color deepened and gave a firm, cracky, leather of poor color. Bisulfiting was also carried out at 3 per cent and 6 per cent for 5 hours at 85°C.

and similar results were obtained. Analyses of the leathers are given. From these latter tests it was concluded that 3 per cent bisulfite was about optimum for color but that bisulfite did not "sweeten" the extract as had been hoped. Studies were then made of mixtures of this extract with "sweetened" chestnut at varying temperatures and the leathers so obtained were examined. The results indicated that such blends could be used satisfactorily. It is also noted that, whereas sideroxylon extract is astringent, it is difficult to get complete detannization of analytical solutions; this difficulty disappears when the extract is bisulfited 3 per cent. A. N. K.

Attempts at Sweetening Chestnut. By P. Chambard and F. Abadie. Bull. *Assoc. Franc. Chim. Inds. Cuir.* **12,** 211 (1950). Sweetening was carried out: (I) with trisodium phosphate and ammonia; (II) with sulfite and bisulfite; (III) with sulfite, bisulfite and ammonia; (IV) with sulfite, bisulfite, ammonia and hydrosulfite. The extracts obtained were examined for color, viscosity, pH and rH, tannage tests. The order of decreasing color was I, Control, III, II, IV. The order of decreasing viscosity was II, Control = I, III, IV. The order of decreasing pH was I, III, IV, II, Control, and the pH decreased with aging in approximately the same order. rH was similar for all except that, on aging, that of I fell rather abruptly and then rose; a similar effect was observed during tannage. On the leathers, color decreased in the order Control, I, III, II, IV, while degree of tannage decreased in the order control (73), II = III, IV, I (49); in all cases sweetening gave more rapid penetration. It was concluded that the sulfite was preferable to phosphate for sweetening. Formulae are given of the various treatments. A comparison of IV with two commercial sweetened extracts indicated it to be very satisfactory. A. N. K.

Use of Merpin in the Strasbourg Leather and Hide Market. By Anon. Bull. *Assoc. Franc. Chim. Inds. Cuir.* **12,** 221 (1950). Studies made on the proper application of Merpin (a disinfectant) to hides and skins. Best results were obtained when 1 part of Merpin Green No. WS Extra 40 was dissolved in 2 parts of water and atomized at a pressure of 1.5 kg. as soon as possible after slaying and before salting. 1 per cent of Merpin is recommended per 100 kg. of raw hides. The rapidity with which micro-organisms attack unprotected hide is stressed. A. N. K.

Hard Chrome Plating in the Leather Industry. By E. Gillet. *Rev. Tech. Inds. Cuir.* **42,** 223 (1950). The characteristics of such platings; their advantages, disadvantages and methods of application are discussed. Their use on rolls and calendars and on press-plates is suggested. A. N. K.

Stream Pollution by Industrial Wastes: Legislation and Treatments. By P. Gourlay. *Rev. Tech. Inds. Cuir.* **42,** 225 (1950). Continued from ibid **42,** 190 (1950). [See abstract *This Journal* **48,** 448 (1953)]. A detailed statement of the requirements listed by the French Department of Public Hygiene. Then follows a discussion of a number of approaches which have been made by various investigators. The complex nature of tannery wastes is pointed out. A. N. K.

Tannery Drums of Modern Construction. By P. Gourlay. *Rev. Tech. Inds. Cuir.* **42,** 230 (1950). A description of water-tight doors, variable speed control and automatic temperature control systems on exhibition at the Leather Week in Paris. A. N. K.

Biochemical Oxygen Demand (B.O.D.) and Its Determination. By P. Chambard and J. Boidin. Bull. *Assoc. Franc. Chim. Inds. Cuir.* **13,** 9 (1951). It is shown that polluted waters absorb oxygen in two stages, the first corresponding to the breakdown of nitrogenous material into ammonia, and of humic acids, etc., to CO_2; the second stage corresponds to the oxidation of ammonia to nitrites and nitrates. This latter does not start until the first is practically complete—usually after 20 days—and may safely be ignored. A formula is given whereby the determination of the 3-day and 5-day oxygen consumption enables the total oxygen consumption of the first stage to be calculated. Methods of sampling and the necessary precautions are discussed; also the preparation of the sample, especially (1) preliminary neutralization, (2) seeding, (3) removal of insoluble matter, and (4) removal of sulfides, sulfites and hydrosulfites which would otherwise falsify the results. The method of B.O.D. determination (modified Winkler) is described. Examples are given, also the calculation of the total (1st stage) oxygen consumption. Sources of error and, finally, the self-purifying capacity of watercourses are discussed. A. N. K.

Report of the (French) Hide Powder Committee. Bull. *Assoc. Franc. Chim. Inds. Cuir.* **13,** 18 (1951). A comparision between the new powder EFT5 and powders EFT3 and EFT4. The new powder was considered acceptable. A. N. K.

Degreasing of Skins in the Fur-Dressing Industry. By M. Voyer. *Rev. Tech. Inds. Cuir.* **43,** 1 (1951). After the furs are tanned and oiled, the excess oil must be removed and the details of this are given. Apart from mechanical dangers inherent in the process, one of the biggest dangers arises from the effect of the vapors, of the solvents used, on the workmen. Means of overcoming this danger are discussed. A. N. K.

Tannage Without Tannin. By P. Saint-Priest. *Rev. Tech. Inds. Cuir.* **43,** 5 (1951). The third of a series [See abstracts *This Journal* **48,** 112 and 449 (1953)]. The increasing difficulty of obtaining vegetable tanning materials and the competition of plastics, especially in the U.S.A., are discussed. The advantages accruing from tannage with resins, as outlined in the earlier papers of this series, are discussed. A. N. K.

An Instrument for Determining Moisture Content. *Rev. Tech. Inds. Cuir.* **43,** 10 (1951). The apparatus consists essentially of a balance on which the sample is placed and subjected to light from an infra-red lamp. With grain, etc., the moisture content can be determined in 20 minutes. A. N. K.

Contribution to the Study of the Green and Violet Modifications of the Salts of the Sesquioxides of Chromium. By E. Justin-Mueller. *Rev. Tech Ind. Cuir* **42,** 181 (1910). Studies indicate that (1) the pH of the salts of Cr sesquioxides is the same (pH-1.5) in the cold as when hot (80-90°C), (2) the color of these salts, excepting the fluoride, is blue-violet in the cold and green when warm, (3) hydration or dehydration does not change the tone though fineness of sub-division affects the intensity. Studies were also made on the effect of basicity and it was found that addition of Na_2CO_3 changed the blue of chrome alum to a green. Whereas the green, heated, solutions slowly revert to the blue-violet, solutions made green with Na_2CO_3 remain green and only become blue-violet (slowly) when sufficient H_2SO_4 is re-added. It is concluded that the green modifications

of the salts of Cr sesquioxides are the result of an internal molecular transposition of the violet salts: this can be obtained either by changing the temperature or by changing the basicity. A.N.K.

On the Permeability of Sole Leathers of Slow and Rapid Tannage. By A. Dohogne. *Rev. Tech Ind. Cuir*, **42**, 185 (1950). Static permeability measurements were made in apparatus described by the author J.I.C.I.C. March 1935) on pieces of sheep and calf skin and on cow hide, all in the white, using (a) distilled water (pH approx 6.0) and (b) Acetic acid solution (pH approx 3.5). It is shown that the swelling action of (b) reduces the permeability very considerably. After 40 hours as above, the solutions were replaced by a 1° Be′ quebracho liquor and, again, the swollen stock had a very much reduced permeability. The appearance of the liquid passing through, and of the different layers of the "tanned" stock was noted. Finally, sole leather of slow tannage (I) and rapid tannage (II), both rolled and not rolled, was tested. After being tested, the samples were washed free of soluble matter, dried, and again tested. The data obtained are tabulated: (1) For the "as is" leather, permeability of II is very much lower than of I. The liquid passing thro' II was very dark and concentrated while that from I was dark but of low density. (2) After removal of soluble matter, both tannages showed increased permeability but II was very much higher than I. (3) It is suggested that the differences in the above are due to the rapid tannage taking place at pH 4-5 so that it contains inter-fibrillary spaces which, after removal of the soluble matter with which they are filled, allows of rapid passage of water. With slow tannage, the pH is lower (around 3.5) and the only interfibrillary spaces are due to the small shrinkage of the fibers during tannage; these, containing only a small amount of soluble matter, give a definite initial permeability. (4) Penetration of tannin is slower by the cold method but the use of very strong liquors (6°-10° Be′) in the later stages of the rapid method prevents fiber-swelling. (5) To improve (reduce) the permeability of II, it is necessary to operate with weaker liquors and lower pH values and it is suggested that the rapid penetration of quebracho (pH-5) compared with chestnut (pH-3) is due to the pH. This is in line with studies on turgescence made by Pothier (Cuir Tech. 15-11-35). (6) Every sole leather tanner should use pH values, in his early liquors, which will give the leather the least permeability, thereby improving the quality which should be his goal. (7) In the wet state, I is the more rigid and this is of importance in walking. (8) Rolling, or hammering, reduces the permeability of I and II, as might be expected, due to reduction in interfibrillary spaces. A.N.K.

Stream Pollution by the Discharge of Waste Waters, Legal Measures and Preventative Treatments. By P. Gourlay. *Rev. Tech. Ind. Cuir* **42**, 190 (1950). A review of recent legislation in France, England and U. S. A. on the subject of the prevention of stream pollution. A.N.K.

BALANCED PERFORMANCE

...and with NOPCOLENES that means surface lubrication with controlled penetration

THE WHITE HORSES of the tradition-rich Vienna Riding School are world-famous. Their ability to execute intricate steps, and pose gracefully, thrills all who see them in action. Here is man utilizing horse sense to get remarkable results. Here is *dual action* achieving *balanced performance* that's tops.

And, in the tanning industry, working with skins and hides, man is applying "horse sense", too—by using *dual action* Nopcolene fatliquors to produce leather with just the surface feel, hand, stretch, break and stitch tear desired . . . leather that's tops for its intended use.

The secret of Nopcolenes' success lies in their unique *double action* which provides superb surface lubrication with carefully controlled penetration—a *balanced performance* that assures the kind of leather products that lead to greater profit and prestige for the tanner.

If you're not already using Nopcolenes, give them a trial. You'll find that they not only do a double-duty fatliquoring job, but offer other important advantages. For example, many Nopcolenes are moisture-free, others contain not more than 6–7% moisture. This means you save on freight, handling and storage. What's more, Nopcolenes are *readily soluble*. We'll gladly send you full information.

FREE! This book gives up-to-the minute data about Nopco's Nopcolene® fat-liquors and formulas for various leathers. Write for a copy.

NOPCO

Chemical Company, Harrison, N. J.

NOPCO — EVOLVED THRU RESEARCH

Branches: Boston · Chicago · Cedartown, Ga. · Richmond, Calif.

Sterozol

Reliable Germicide and Preservative

Sterozol is a non-coloring, non-interfering liquid which can be used in any wet operation:

- For inhibiting microbial action on hides and skins in process
- For inhibiting mold on stock and leather in process
- For preserving finishes

Sterozol's low relative toxicity, ease of handling, and economy have contributed in a large measure to its acceptance in the trade.

Sebacol

. . . for dependable unhairing

Sebacol produces clean, uniform, quality leather under varied beamhouse practices.

Biobate

. . . for effective baiting

Biobate provides controlled, effective enzymatic action during baiting for all types of leather.

WALLERSTEIN COMPANY, INC.

180 MADISON AVENUE • NEW YORK 16, N. Y.

TYPICAL ANALYSIS OF BARIUM'S

SODIUM SULPHIDE FLAKES

Fe	0.0005%
Other Heavy Metals	Nil
Na Cl	0.40
Other Na_2O (not oxidizable)	1.35
Na_2S	61.00

Manufactured in large tonnages by

BARIUM REDUCTION CORPORATION

SOUTH CHARLESTON 3, WEST VIRGINIA

need we say more?

BORNEO **CUTCH** EXTRACT
(MANGROVE BARK EXTRACT)
SAXE CUTCH CORPORATION
500 FIFTH AVENUE NEW YORK 36, N. Y.

UNIFORM TANNER'S OILS
for Every Type of Leather
MARDEN WILD CORPORATION
SOMERVILLE, MASSACHUSETTS
MARDEN WILD OF CANADA, LTD., HALIFAX, N. S.

LIGHT, EVEN-COLORED LEATHER

Many leather-processing men have found they can consistently get light, even-colored leather by standardizing on Sun's "Job Proved" Leather-Processing Oils. These oils mix easily. They do not form surface scum. They make it possible for the tanner to maintain uniformly high quality. They make it possible to process leather without frequent delays. For additional information, call your nearest Sun Office . . . or write to SUN OIL COMPANY, Philadelphia 3, Pa. *In Canada:* Sun Oil Company, Ltd., Toronto and Montreal.

SUN PETROLEUM PRODUCTS SUNOCO
"JOB PROVED" IN EVERY INDUSTRY

Warner

BELL-MINE LIME

Year-round Uniformity
Dependable Source of Supply

WARNER COMPANY

Bellefonte Division, Bellefonte, Pa.

PITTSBURGH - - - - PHILADELPHIA - - - - NEW YORK

THE OHIO LEATHER CO.

LUXOR CALF COLORS **BLACK JETTA CALF**
WASHETTE • WHITE AND COLORS

TANNERY & GENERAL OFFICES: GIRARD, OHIO
BOSTON • NEW YORK • ST. LOUIS • CHICAGO

EISENDRATH FINE CALF LEATHERS

IN COLORS AND BLACK

B. D. Eisendrath Tanning Company

801 Merchandise Mart, Chicago, Ill. • Tannery at Racine, Wisconsin

92 South St., Boston, Mass., Day Gormley Leather Co. 12 E. 33rd St., New York City, Moe Shapiro

MORITE BRAND
EST. 1908
MORITE BRAND
Sulphonated and Compounded
OILS
MORITE BRAND
EST. 1908
WHITTEMORE-WRIGHT COMPANY, INC.
62 ALFORD ST. CHARLESTOWN DISTRICT BOSTON, MASS.

PRESTO
The Original Dry Color
for Splits and Suede
(also in paste form)
PRESTO COLOR COMPANY
WEST ALLIS 14, WIS.
Dry Colors ❖ ❖ Finishes

when you want
BORAX AND BORIC ACID HAVE LONG BEEN USED IN THE TANNING AND FINISHING OF GOOD LEATHER
borax or **boric acid**
think first of
SEND TODAY FOR FREE BOOKLET: "PROCESSING HEAVY LEATHER"
PACIFIC COAST BORAX CO.
DIVISION OF BORAX CONSOLIDATED, LIMITED
NEW YORK • LOS ANGELES • CLEVELAND • CHICAGO
Distributors located in principal cities throughout the U.S.A.

MANUFACTURERS OF FAMOUS "20 MULE TEAM" PACKAGE PRODUCTS

REILLY-WHITEMAN-WALTON CO.

OILS of CHARACTER

CONSHOHOCKEN, PA.

THE LEATHER MANUFACTURER

ESTABLISHED 1883

Exclusively a Tannery Paper

Devoted to Leather Technology, Tanning and Finishing of Leather, Tannery News and Markets.

Affords complete tannery coverage, concentrated among tanners, chemists and buyers of materials, raw stock and equipment.

Technical articles and newsworthy features invited for publication.

THE LEATHER MANUFACTURER

NEW YORK OFFICE
154 Nassau St.

BOSTON OFFICE
683 Atlantic Ave.

DIRECT ROUTE INTO TANNERIES

Shoe and Leather REPORTER

TANNERY BUYER

THE TECHNICAL JOURNAL FOR SUPERINTENDENTS, CHEMISTS, TANNERS AND BUYERS

The TANNERY BUYER Section of the *Shoe and Leather Reporter* is published the third issue every month and is read by every important executive, superintendent, chemist and buyer.

Tell your message to these men who buy your product in the TANNERY BUYER.

SHOE AND LEATHER REPORTER

Executive Offices: 210 LINCOLN ST., BOSTON 11, MASS.

Representatives in

CHICAGO • LONDON, ENG. • PHILADELPHIA • WASHINGTON
ST. LOUIS • NEW YORK • LOS ANGELES • SAN FRANCISCO

Salem Oil & Grease Co.

FAT LIQUORS

FEATURING

CONTROLLED PENETRATION

●

SALEM, MASSACHUSETTS

STANDARD HIDE POWDER

A material made to specifications and used internationally for the analysis of vegetable tanning materials

FRANK F. MARSHALL
RIDGWAY · PENNSYLVANIA

Garden State Tanning Inc.
Pine Grove, Pa.

Manufacturers of
Upholstery Leather

New York Office **330 Fifth Avenue**

Tanolin®
DIAMOND ALKALI CHEMICALS®
Best Known—Most Used One Bath Chrome Tan
DIAMOND ALKALI CO.
CLEVELAND 14, OHIO

KEPEC FINISHES · KCC CHEMICALS

KEPECO EMULLO FINNALINE KEEPA-SHINE UNI-LAK (Reg. U. S. Pat. Office) KEPOLAC FONDO

KEPEC CHEMICAL CORPORATION
Milwaukee 1, Wisconsin

A·S·K TRADE MARK

ARTHUR C. TRASK CO.
Tanners Oils & Extracts
CHICAGO, ILL.
4103 S. LASALLE ST.

. . . . . LET'S GET THE ANSWERS ABOUT MAGAZINE LEADERSHIP in the Tanning Industry...

Which magazine does the outstanding job in editorial service?
Which magazine has 101% more paid and audited circulation?
Which magazine carries more than 100% more advertising?

Tanning industry executives know that only in Leather and Shoes do they get the complete and timely job in news, markets, features, and editorial service.

Complete and often *exclusive* coverage of technological progress in tanning methods and production, supplies, materials, equipment and machinery, *plus* the facts about demand, markets, uses, and trends in the leather-using division of the industry, *plus* the keenest, most thought-provoking editorials on the leading problems and interests of the entire field.

Because they get the fullest measure of service each week, tanning executives subscribe to L & S at a 100% higher rate than to the second paper —almost 2 to 1 leadership.

This leads naturally to greater productivity for advertisers who respond with the greatest volume of advertising. L & S carries 124% more tanning material, chemical, oil, etc., advertising than the second paper, and 117% more tanning machinery and supply advertising.

That's the story about magazine leadership in the tanning industry. It's L & S all the way. If you want more facts, write us today.

L&S

LEATHER AND SHOES
300 W. ADAMS STREET
CHICAGO 6, ILLINOIS

Finishes
for all types of
Leather

FINE LEATHER FINISHES
NLF

NEWARK
LEATHER FINISH CO.

8 WILHELM ST. HARRISON, N. J.
Telephone: Humboldt 5-3470

HOWES LEATHER CO. INC.
SOLE LEATHER
•
Tanners Cut Sole Division
•
CUT SOLES

BOSTON, MASS.
ST. LOUIS, MO. CHICAGO, ILL.

BONA ALLEN, INC.
Buford, Georgia
TANNERS SINCE 1873
•
Finest English Rein
and Strap Leather
Latigotan Harness Leather
Manufacturers of genuine English
type and full rigged hand tooled
roping saddles.

LEDOGA S.p.A.

FOUNDED 1868

LEDOGA

Garressio-One of the 22 Italian plants controlled by Ledoga S.p.A.

WORLD'S LARGEST PRODUCERS OF

CHESTNUT EXTRACTS

Produced in *Italy*

Types: • Regular spray-dried powdered Chestnut Extracts • "Dulcotan", a sweetened Chestnut Extract as a Quebracho substitute

Properties: Highly Concentrated • Double Decolorized • Very Light Colored • Great Purity (due to very low non-tannin contents)

LEDOGA S.p.A. sells the total production of 22 of the 38 plants in Italy making Chestnut Extract.

*

Barkey

Importing Co., Inc.

44 East 53rd Street, New York 22, N. Y.

Exclusive Representative in the United States and Canada

TANIMEX CORP.

350 FIFTH AVENUE., NEW YORK, N. Y.

PRIME IMPORTERS OF

QUEBRACHO

and

WATTLE EXTRACTS

in solid form

We have available Quebracho Extract, Wattle Extract, Myrabolam Extract in concentrated spray dried form.

Also Raw Tanning Materials of all descriptions.

Always Foremost

Armour's QUALITY Leathers USA

Sole and Upper Leather

●

ARMOUR LEATHER CO.

Chicago Boston New York

New leather quality—yours with *Nitrex!*

Now—thanks to this specially developed butadiene-acrylonitrile latex for leather treatment—you can give your leather products great new selling features, with new ease of finishing!

New toughness and durability! With its high tensile strength, Nitrex® gives leather outstanding resistance to tearing, scuffing, all sorts of abrasion. It protects against water, gasoline and other petroleum products, animal fats and oils, alcohols, glycols, paint and ink dryers, and lacquer solvents—keeps leather soft, supple, and strong under the severest conditions.

New good looks! Nitrex is completely non-staining. It gives glossy, tack-free finishes that may be either transparent or opaque, in a wide variety of true, lasting colors. What's more, Nitrex-coated leather has excellent resistance to sunlight and aging—won't craze, dull, or lose its beauty for years and years.

New ease of application! Since Nitrex is a water dispersion, it accepts fast acceleration without scorching. And it is highly compatible with casein.

See how easy it is to treat *your* leather products to new beauty and serviceability. To learn more about Naugatuck's Nitrex, its use and many advantages, simply write on your letterhead to the address below. Nitrex is a product of the world's leader in latices.

Naugatuck Chemical

Division of **UNITED STATES RUBBER COMPANY** • 356 Elm Street, Naugatuck, Conn.

BRANCHES: Akron • Boston • Charlotte • Chicago • Los Angeles • Memphis
New York • Philadelphia **IN CANADA:** Naugatuck Chemicals, Elmira, Ontario

"The Extension of Knowledge is by the Investigation of Matter".

This space dedicated to
Tanners' Council Research Laboratory
by a Friend

RESEARCH
has Two functions
To produce a better Product and to do it More Economically.

THE TANNERS' COUNCIL RESEARCH LABORATORY
UNIVERSITY OF CINCINNATI

THE TANNERS' COUNCIL RESEARCH LABORATORY
University of Cincinnati

We serve the Tanning and Leather Industry through a broad program of Research.

RESEARCH PAYS DIVIDENDS
when Properly Applied.

THE TANNER'S COUNCIL RESEARCH LABORATORY
Universtty of Cincinnati

WHEN
YOU
BUY
TANNERS'
CORN SUGARS
CORN SYRUP
CORN STARCH
LACTIC ACID
REMEMBER

CLINTON

CLINTON FOODS INC.
CLINTON, IOWA

THE
TANNERS' COUNCIL RESEARCH LABORATORY

at

THE UNIVERSITY OF CINCINNATI

is

THE DEPARTMENT OF BASIC SCIENCE

in

THE GRADUATE SCHOOL OF ARTS AND SCIENCE

The purpose of the laboratory is to conduct scientific research in the fields of Science concerned with Tanning and Leather.

To train Chemists in the technique of research and prepare them for Industry.

This Laboratory serves as the Official Technical Headquarters for the Tanning Industry of the United States.

Your inquiries will be gladly answered.

Address DR. FRED O'FLAHERTY, Director
Tanners' Council Laboratory
University of Cincinnati
Cincinnati 21, Ohio.

TANNERS! Now Available . . .

REQUESTED SHORT TERM COURSES

IN SPECIFIC PHASE STUDIES

COLORING
FAT LIQUORING
FINISHING

Especially designed for industry personnel; includes Beamhouse work.

FIRST COURSE COMMENCES SEPTEMBER 17TH

ALSO

REGULAR LONG TERM PROGRAMS — 3 Terms for High School Graduates; 2 Terms for College Graduates

Sponsored by Tanning & Allied Industries • Approved by Tanners' Council of America, Inc.

SCHOOL OF LEATHER & TANNING TECHNOLOGY

PRATT INSTITUTE • BROOKLYN 5, N. Y.

Write for literature and application form.

Fill in and Mail →

NAME _____

ADDRESS _____

CITY & STATE _____

INDEX TO ADVERTISERS

AMERICAN CYANAMID COMPANY V
AMERICAN DYEWOOD CO. X
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XIX
ARKANSAS COMPANY, INC. VI
ARMOUR LEATHER CO. XXXV
ARTHUR C. TRASK CO. XXXI
ARTHUR THOMAS CO. XXII
ATLAS REFINERY VII
BARKEY IMPORTING CO., INC. XXXIV
BARIUM REDUCTION CORPORATION XXV
BONA ALLEN, INC. XXXIII
BORNE, SCRYMSER COMPANY XVI
BUCKMAN LABORATORIES, INC. XVII
CHEMTAN COMPANY XXI
CLINTON FOODS INC. XXXVI
DIAMOND ALKALI CO. XXXI
EISENDRATH TANNING CO. XXVII
FRANK F. MARSHALL XXXI
GARDEN STATE TANNING INC. XXXI
GENERAL DYESTUFF CORPORATION IX
HOOKER ELECTROCHEMICAL CO. XVIII
HOWES LEATHER CO., INC. XXXIII
INTERNATIONAL PRODUCTS CORP. XII
KEPEC CHEMICAL CORPORATION XXXI
LEATHER AND SHOES XXXII
LEATHER MANUFACTURER, THE XXIX
L. H. LINCOLN & SON, INC. IV
MARDEN WILD CORPORATION XXVI
MEAD CORPORATION, THE XIII
NEWARK LEATHER FINISH CO. XXXIII
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXVII
OLSON SALES AGENCY, THE ..... Inside Front Cover
PACIFIC COAST BORAX CO. XXVIII
PRESTO COLOR CO. XXVIII
REILLY-WHITEMAN-WALTON CO. XXIX
RIVER PLATE CORPORATION, THE XIV
ROBESON PROCESS CO. II
ROHM & HAAS XV
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXVI
SCHOOL OF LEATHER & TANNING TECHNOLOGY XXXVIII
SHOE & LEATHER REPORTER XXX
SOCONY-VACUUM OIL CO. I
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. XI
SUN OIL COMPANY XXVI
TANEXCO, INC. ..... XL—Inside Back Cover
TANNERS' COUNCIL RESEARCH LABORATORY ..... XXXVII—XXXVIII
TANIMEX CORPORATION XXXV
TEAS EXTRACT CO. III
UNION STARCH & REFINING CO. XIX
UNITED STATES RUBBER COMPANY XXXVI
WALLERSTEIN COMPANY, INC. XXIV
WARNER CO. XXVII
WHITTEMORE-WRIGHT CO. XXVIII
WOLF, JACQUES & CO. VIII
YOUNG CO., J. S. XX

ITALIAN

CHESTNUT EXTRACT

SOLID — POWDER — SPRAY DRIED

MADE FROM LIVE WOOD

TYPICAL A.L.C.A. ANALYSIS

	Solid	Powder	Spray Dried
TANNIN	61.72	66.7	73.5
NON-TANNIN	21.65	21.2	19.1
INSOLUBLES	.65	.6	.7
WATER	15.98	11.5	6.7
ASH	.67	.82	.75

STAINLESS SUMAC CRYSTALS

HIGHEST QUALITY—MADE UNDER THE SUPERVISION OF THE WORLD'S LEADING EXTRACT CHEMISTS

TANEXCO, INC.

549 W. Washington Blvd. Chicago, Illinois

MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

TANNIN	61.55
NON-TANNIN	16.03
INSOLUBLES	1.70
WATER	20.72

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

For further information address:

TANEXCO, INC.

549 WEST WASHINGTON BLVD., CHICAGO 6, ILLINOIS

SOLE AGENTS
U. S. A.

DERMABATE COMPOUNDS LIQUID EXTRACTS

HEMLOCK
OAK
MANGROVE
WATTLE
STAINLESS SUMAC
ORDINARY SUMAC
QUEBRACHO
SPECIAL DIPPING EXTRACTS
RAPID TAN "G"

★

AMERICAN EXTRACT CO.

Manufacturers of the Largest
Variety of Vegetable Tanning Extracts
Established 1887
PORT ALLEGANY, PA.

CANADIAN REPRESENTATIVES:
McArthur Chemical Co., Ltd., 20 St. Paul St., West, Montreal: 73 King St., West Toronto
ENGLISH REPRESENTATIVES:
Roy Wilson, Dickson, Ltd., 7-8 Railway Approach, London, S. E. 1